RANDOLPH

THE MAGNETIC PROPERTIES OF SOME RARE EARTH OXIDES AS A FUNCTION OF THE TEMPERATURE.

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BY

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B. S. Missouri School of Mines, 1911
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THESIS

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I HEREBY RECOMMEND THAT THE THESIS PREPARED UNDER MY SUPERVISION BY OSCAR ALAN RANDOLPH

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BE ACCEPTED AS FULFILLING THIS PART OF THE REQUIREMENTS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN PHYSICS

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I INTRODUCTION

Practically all of the rare earth elements and compounds bear a close chemical and physical relationship. They may be thought of as forming a band in the periodic table extending from cerium in Group IV to tantalum in Group V, since both their chemical and physical properties vary in a continuous manner. They are like the alkaline earths in that their metals are white in color and decompose cold water slowly. Their oxides are strongly basic. They are like aluminum in that they form trivalent salts.

The chemical similarity of the rare earths makes their separation in many cases an exceedingly long and careful process. The only method available in many cases is that of fractional precipitation or fractional crystallization, a process which must be repeated in some cases several thousand times before material of high purity is obtained.

The method of separation has divided the rare earths into groups and it will be noted that this grouping is in accordance with the sequence of the atomic weights.

	Element	Symbol	Atomic Weight	Color of Salts
Yttrium group	(Scandium	Sc	44.1	colorless
	(Yttrium	Yt	89.0	colorless
Cerium group	(Lanthanium	La	139.0	colorless
	(Cerium	Ce	140.25	cerous,colorless;ceric, orange to red
	(Praseodymium	Pr	140.6	green
	(Neodymium	Nd	144.3	red to reddish violet
	(Samarium	Sa	150.4	topaz yellow
Terbium group	(Europium	Eu	152.0	faint rose
	(Gadolinium	Gd	157.3	colorless
	(Terbium	Tb	159.2	colorless

	Element	Symbol	Atomic Weight	Color of Salts
Erbium group	(Dysprosium	Dy	162.5	bright green
	(Holmium	Ho	163.5	yellow to orange
	(Erbium	Er	167.7	deep rose
	(Thulium	Tm	168.5	bluish green
Ytterbium group	(Ytterbium	Yb	172.0	colorless
	(Lutecium	Lu	174.0	colorless
	(Celtium	-	---	----

Their most important physical properties are shown by their spectra. The absorption spectra are of value with those elements which form colored salts, such for example, as praseodymium and erbium. The absorption bands are well defined, have sharp edges and can be observed in very dilute solutions. The spark spectra are quite characteristic in many cases and the arc spectra are of the highest importance in testing for purity and in following the effect of fractional precipitation or fractional crystallization. In the latter case it is only necessary to watch the weakening or strengthening of certain lines, and this can be done without a knowledge of the complete spectra.

A rather interesting property is that of the phosphorescence produced by cathode rays impinging upon certain mixtures of rare earths. This phosphorescent light is characteristic of the composition of the sample but the effect is too sensitive to be of much practical use. As little as one millionth part of a colored earth is enough to produce phosphorescence in a colorless earth.

The magnetic properties are of prime importance and the susceptibility varies so markedly between certain elements that it forms a good criterion of their purity. Urbain finds a

straight line relationship existing between the composition of a mixture of two rare earth salts and the corresponding susceptibility, and recommends the use of the susceptibility in following the results of a fractionation. As an illustration of the importance of this property it may be well to mention that by it he was led to the discovery of a new element, namely celtium. Some work has been done on the variation of the susceptibility with temperature, but on the whole the field is an open one. It is the purpose of this paper to investigate this variation for the oxides of dysprosium, erbium, gadolinium, holmium, neodymium and ytterbium, in the temperature range 30°C to -160°C, and to consider the data obtained as evidence for or against the existence of the magneton. If Curie's law (the susceptibility times the absolute temperature equals a constant) is found to hold, then it might seem likely that the cause of the magnetism is due to an elementary charge of exactly the same nature in all the materials.

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II THEORY OF METHOD

Curie's method which consists in measuring the pull exerted on an object placed in a nonuniform magnetic field, was the one used. It seemed the most desirable on account of the small amount of material needed to carry out a determination. The theory follows:

If the permeability of air be taken as unity, then the magnetic energy per unit volume at a point where the field strength is H is given by $\frac{H^2}{8\pi}$. If a sample of permeability μ is introduced at this point then the potential energy is changed to $\frac{\mu H^2}{8\pi}$ per unit volume. The work done in placing a sample of volume v at the point in question is $\frac{(\mu-1)H^2}{8\pi} \cdot v$. If we imagine the sample brought in from the x-direction we have the work done equal to $\int F_x dx$ taken between the proper limits.

Hence
$$\int F_x dx = v\frac{(\mu-1)H_y^2}{8\pi}$$

or
$$F_x = \frac{\partial}{\partial x}\left[v \cdot \frac{(\mu-1)H_y^2}{8\pi}\right]$$

$$F_x = \frac{2v(\mu-1)\, H_y\frac{\partial H_y}{\partial x}}{8\pi}$$

$$= \frac{v(\mu-1)H_y\frac{\partial H_y}{\partial x}}{4\pi}$$

Instead of μ we may write its equivalent $1+4\pi k$, where by k we mean the susceptibility per unit volume.

Therefore
$$F_x = v\,\frac{(1+4\pi k-1)}{4\pi}\, H_y\, \frac{\partial H_y}{\partial x}$$

$$= v\; k\; H_y \frac{\partial H_y}{\partial x}$$

If we use the susceptibility per unit mass χ instead of per unit volume, then using the relation $k = \chi d$ where d is the

density of the sample, we get

$$F_x = vd\chi\, H_y \frac{\partial H_y}{\partial x}$$

$$= M\chi\, H_y \frac{\partial H_y}{\partial x}$$

where M represents the mass.

Generally, the force is measured by means of a twist on a suspension. If the couple necessary to twist such a suspension through one radian is c and the lever arm to the sample is l then

$$c\varphi = F_x l$$

where φ is the twist in radians.

$$F_x = \frac{c\varphi}{l}$$

and our fundamental equation becomes

$$\frac{c\varphi}{l} = M\chi H_y \frac{\partial H_y}{\partial x}$$

whence

$$\chi = \frac{1}{M\, H_y \frac{\partial H_y}{\partial x}} \cdot \frac{c\varphi}{l}$$

In the derivation of the above formula it will be noticed that the volume susceptibility of air has been taken as unity, that k and χ have been assumed not to vary with the strength of field, and that H is the magnetic field within the specimen. For diamagnetic and paramagnetic bodies this latter assumption can be made without sensible error. In the case of ferromagnetic substances, however, this point must be investigated and corrected for. Further, if the long axis of the specimen does not lie parallel to the magnetic field an additional correction must be made.

The various factors appearing in the formula for χ were determined as follows: M by a chemical balance sensitive to

$\frac{1}{30}$ of a milligram; H_y and $\frac{\partial H_y}{\partial x}$ by a test coil; c by vibration experiments; φ by reading the position of a reflected beam of light scale distance 104.4 cm.; and l by a cathetometer.

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III DESCRIPTION OF APPARATUS

Magnet:- The magnetic field was produced by a du Bois half-ring electro-magnet, the pole pieces of which were of soft Swedish iron tapered down to a 1 centimeter circular face. The poles of the magnet were turned from their normal position so as to form an obtuse angle of about 172°. The distance between pole pieces was roughly 2.5 centimeters. As it was not found necessary to use a magnetizing current greater than 10 amperes, the changes in the magnetic field due to heating of the magnet were negligible. This point was also tested experimentally.

Test Coil:- The test coil used for measuring the field strength and the variation of the field strength in the x-direction was turned from ebonite. The dimensions in centimeters are given in the accompanying sketch. The coil was carefully wound with number 40 double silk covered magnet wire in two layers, each having twelve turns. The first layer was wound, shellaced and allowed to become almost dry before winding the second. When the second layer was wound the coil was again shellaced and the wires leading from the coil tightly twisted together, first twenty turns were made in one direction, then twenty turns in the other. The object of doing this was to eliminate the effect due to magnetic lines being cut by portions of the circuit other than the test coil.

The coil with its axis horizontal and parallel to the y-direction was mounted at the end of a hard rubber arm 35 centimeters in length. The other end of the arm was secured to a carriage by a horizontal axis about which the arm could swing.

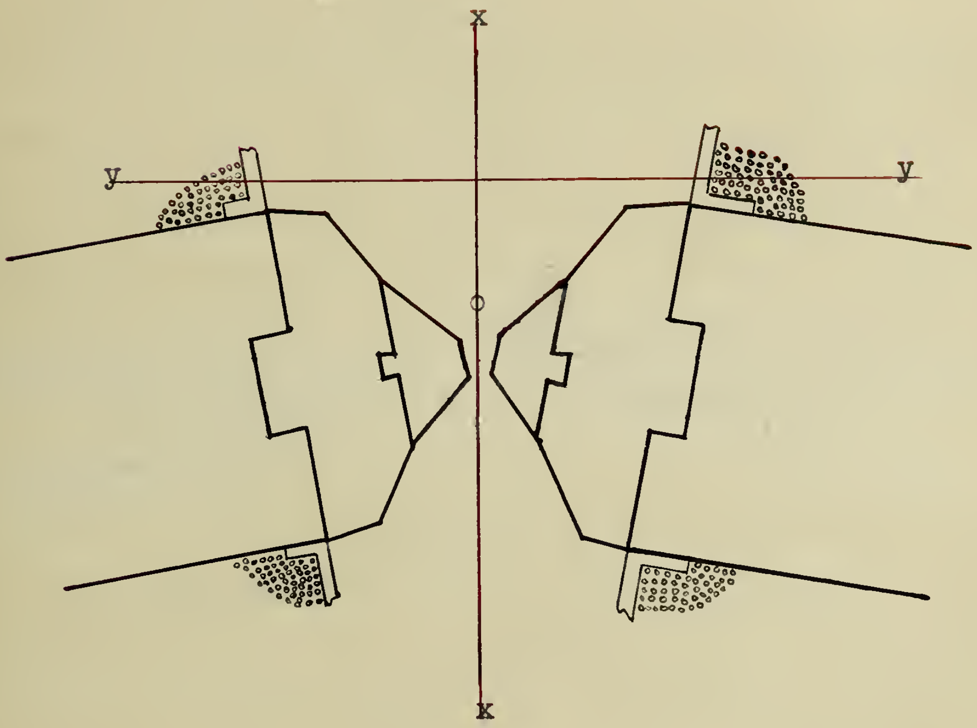

DIAGRAM OF POLE PIECES.

The point marked "o" is the point of maximum $H \frac{\Delta H}{\Delta z}$.

The carriage (and hence the test coil) could be moved in the x-direction by a rack and pinion. Its position was accurately read to within 0.005 centimeters or less by a vernier.

Thermocouple:- A copper advance* wire thermocouple was used. The wires leading to the sample were very approximately 0.0075 centimeters in diameter; the copper wire was double silk covered. On leaving the torsion balance, these wires were soldered to wires of larger diameter.

The ice junction was placed in a large funnel which was filled with shaved ice. The surplus water, accumulated by the melting ice, was drained off by a rubber tube connected to the small end of the funnel and closed by a pinch cock. The junction measuring the temperature of the sample was enclosed in a thin walled capillary tube and the two wires insulated from one another by a still smaller capillary tube inside the first.

During a series of measurements the thermocouple was left in the silica capsule containing the sample. Although it contained highly magnetic nickel it should be borne in mind that the above alloy is not highly magnetic. It was found by trial that the susceptibility measured with the thermocouple in the sample and the susceptibility when measured with the thermocouple removed were the same. The amount to be subtracted from the readings due to the magnetic properties of the system was, of course, greater with the thermocouple than without.

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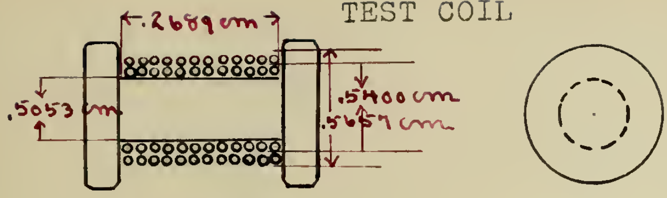
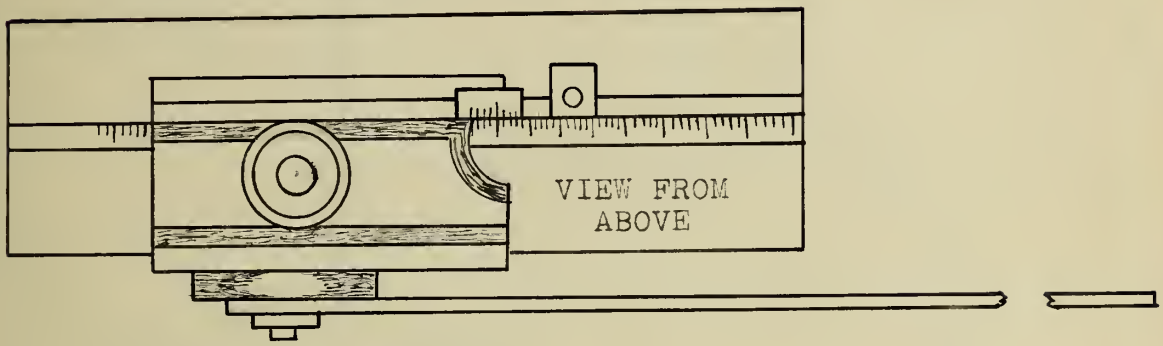
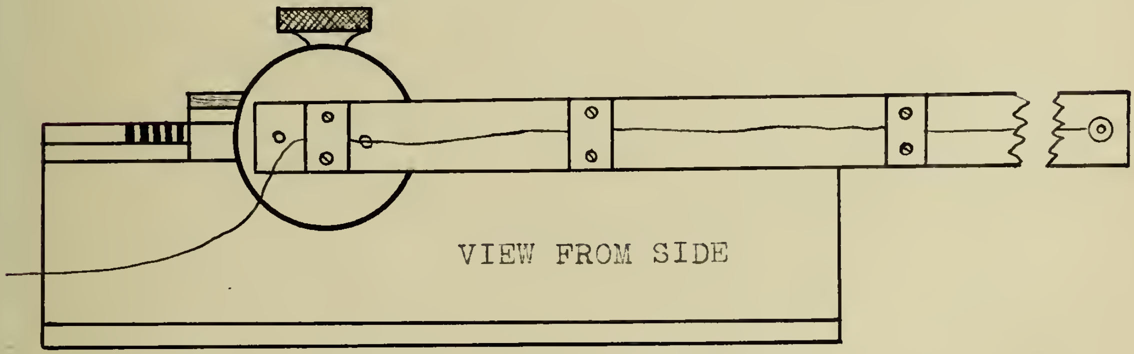
*The advance wire was supplied by the Driver-Harris Wire Company. It behaves practically the same as constantan. Palmer (Phys. Rev. 21, 65 (1905) gives its analysis as copper 55%, nickel 44.4%, iron .6%, and its electromotive force against copper as 50 microvolts per degree.

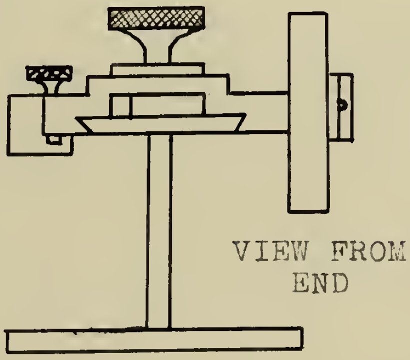
TEST COIL

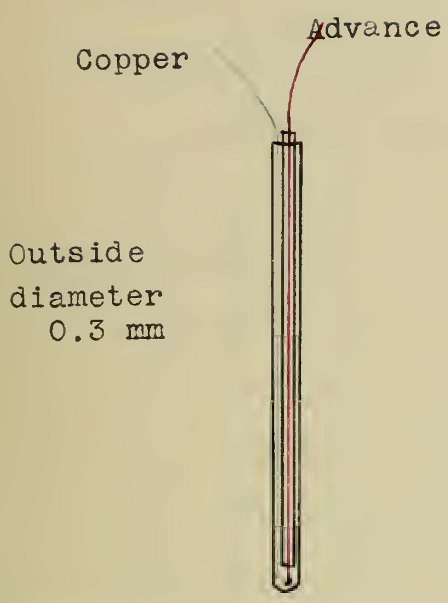


APPARATUS CARRYING TEST COIL

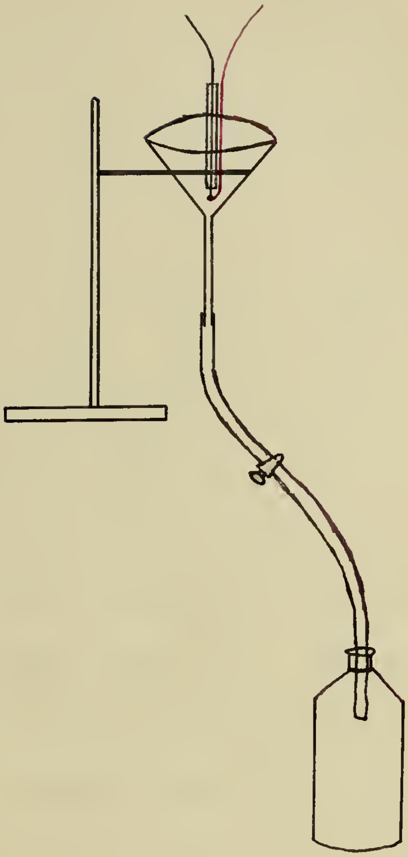




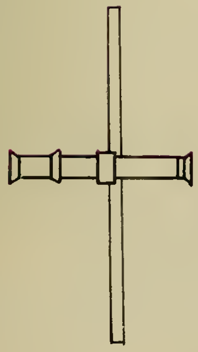


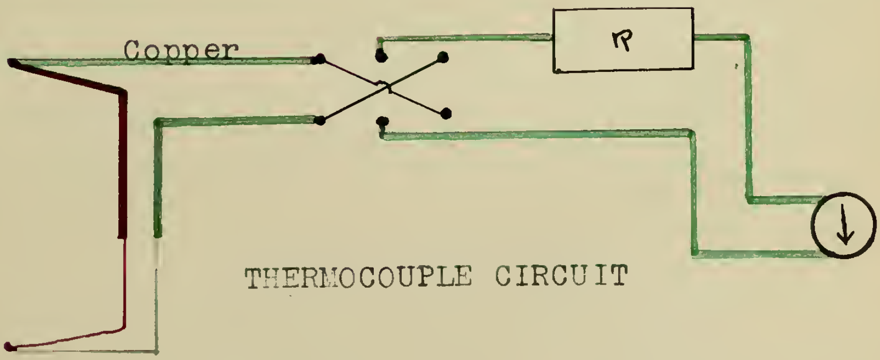


DETAILS OF SMALL THERMAL JUNCTION



ICE JUNCTION OF THERMOCOUPLE





THERMOCOUPLE CIRCUIT

The thermocouple was connected by a reversing switch to a Leeds and Northrup D'Arsonval galvanometer* in series with 2000 ohms. This arrangement gave a deflection of about 1 1/4 scale divisions per degree centigrade for the distance used. (Scale distance 150 centimeters)

Torsion Balance:- The torsion balance was contained in a wooden box put together with wooden pegs. The box was fitted with sliding doors of glass so that the balance was entirely visible. The balance itself consisted of a silver torsion wire about 0.025 centimeters in diameter and 17.68 centimeters long. From it was suspended, an aluminum rod 46 centimeters long bent at right angles at a distance of 10 centimeters from one end. The bent or vertical end of the rod carried an aluminum frame work which in turn carried the silica capsule containing the sample. The capsule was held in place by means of a set screw in the collar "C". The unequal expansion between the aluminum and the silica was allowed for by slitting the collar.

The system was damped by four damping vanes at right angles to each other, each two by one centimeters in size and submerged in glycerine. It was found very essential that these vanes be entirely covered, for if not the effect of surface tension on the exposed part of the vanes was enough to make the readings very erratic.

The upper part of the suspension was connected to a torsion head which could be moved by a tangent screw. The angle through

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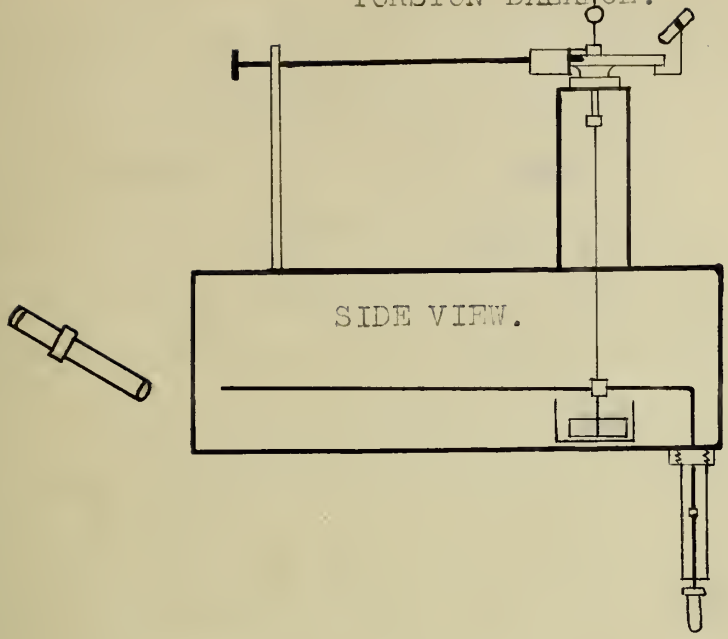
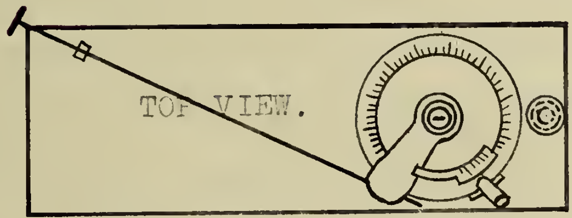
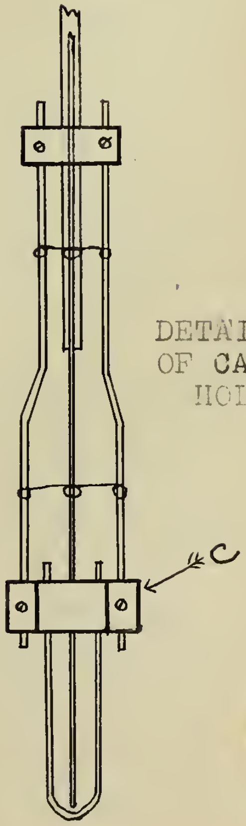
*Galvanometer PL3089B. Resistance 26.65 ohms, figure of merit 1.31 x 10^{-8} amperes /mm. Resistance. Otto Wolff box PL3325A.

TORSION BALANCE.







DETAILS OF CAPSULE HOLDER.

SILICA CAPSULE
FOR CONTAINING SAMPLE.

which the torsion head had been twisted could be read directly in degrees but was generally read by the reflection of a beam of light from a concave mirror rigidly connected to the torsion head and situated directly over the suspension. The distance between scale and mirror was 104.4 centimeters.

The couple acting on the sample was measured by first marking the position of the aluminum pointer with the cross hairs of a telescope and noting the position of the reflected beam of light. The current was then turned on and the torsion head turned until the pointer, and hence the sample, was brought back to the original position and the position of the light beam again noted. The difference between these two readings and the distance of the scale from the mirror gave the necessary data for calculating the angle φ through which the suspension was twisted. This with a knowledge of the constant of the suspension gave the couple. The residual magnetism retained in the magnet when a magnetizing current of 1.5 amperes was broken gave so small a value of $H_y \frac{\partial H_y}{\partial x}$ that no attempt was made to eliminate it. When 5 amperes were used the value was also quite small but this was reduced still smaller by applying a current of the proper magnitude in the reverse direction.

The advantage of this procedure over that of reading the deflection direct by means of the telescope is that the sample is always in the same portion of the field and hence the value of $H_y \frac{\partial H_y}{\partial x}$ does not change.

The thermocouple wires ran from the sample along the aluminum arm of the balance to the point of suspension. For a

greater part of the way they were insulated by capillary glass tubes. The junction itself was so arranged that it could be inserted or taken out of the capsule by a long glass hook. The wires left the balance box by a loose spiral at a point near the upper part of the suspension chamber.

Cooling Device:- The sample was cooled to low temperatures by the method described some time ago by Dr. C. T. Knipp of this laboratory[*]. A copper rod 10 1/2 inches long and 1 inch in diameter was tapered at one end and bored out at the other with a 1/2 inch drill to a depth of 1 1/2 inches. When ready for use the rod was placed in a Dewar bulb and the silica capsule containing the sample placed in the hole at the top. Then the liquid air was added to the bulb as needed. The temperature could be controlled very nicely by depth to which the rod was covered and when desired the temperature could be held practically constant over a considerable length of time. The minimum temperature attainable by this method evidently depends upon the dimensions of the rod and the amount submerged. With the arrangement used it was possible to get within 30° of liquid air temperature.

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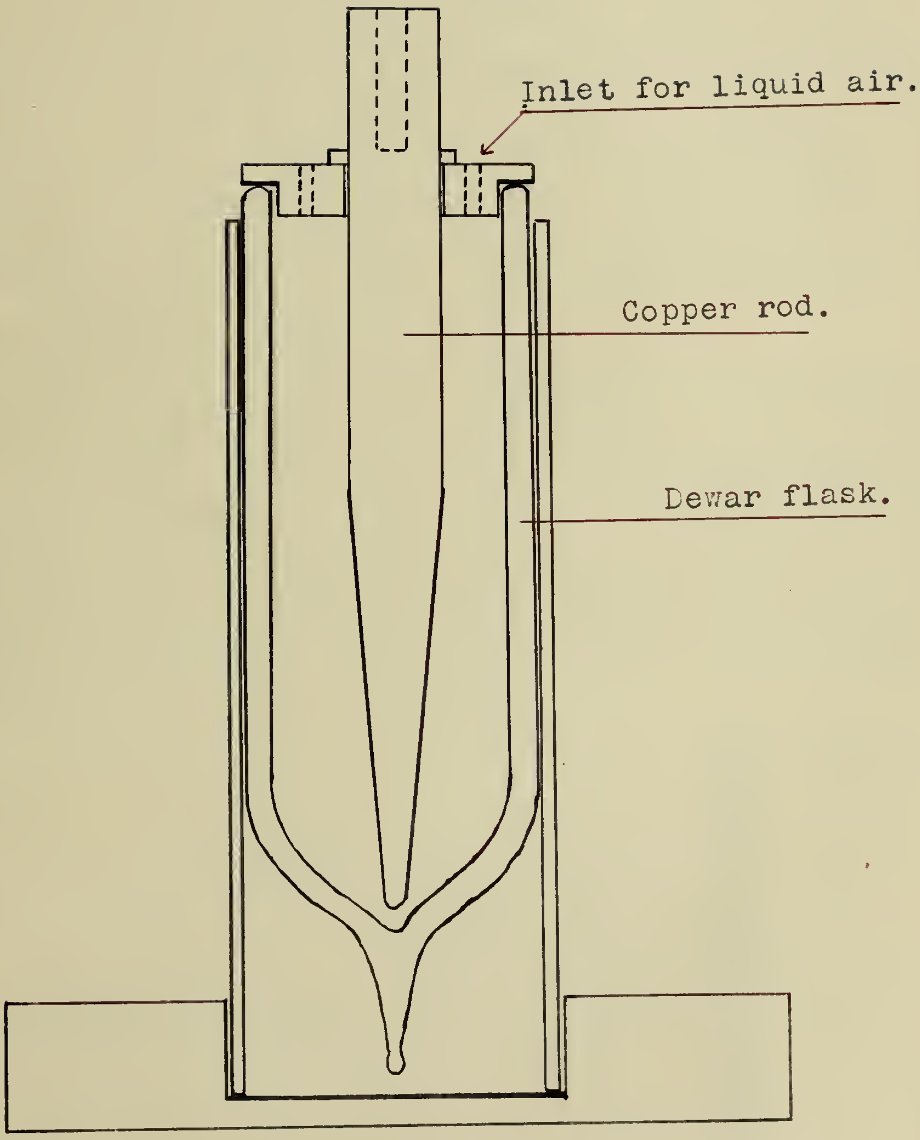
[*] Phys. Rev., 15, 125 (1902)

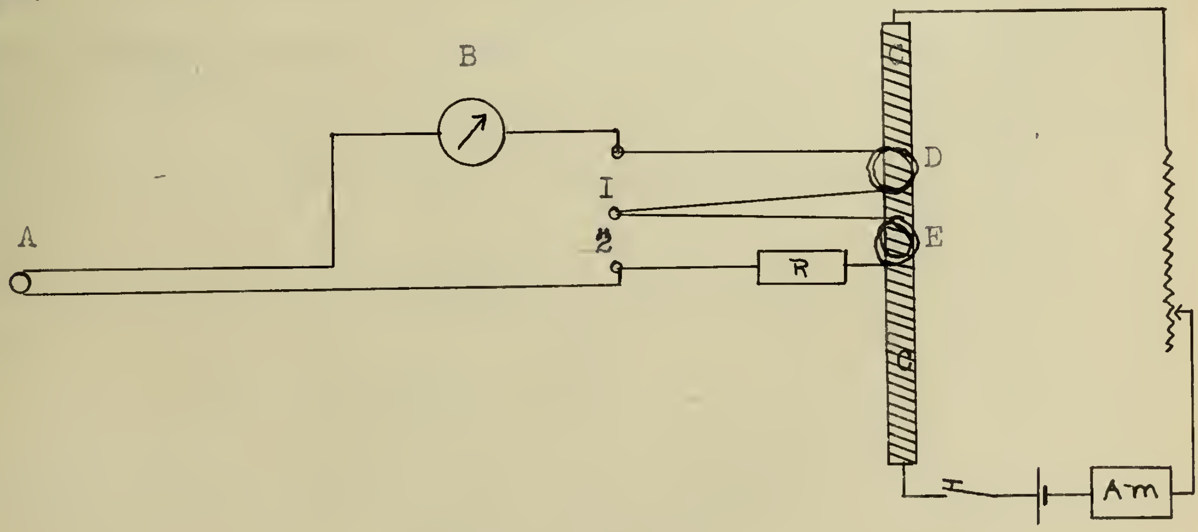


DEVICE FOR OBTAINING LOW TEMPERATURES.

IV CALIBRATIONS

Calibration of Field:- The value of H_y and $\frac{\partial H_y}{\partial x}$ at various points of the field was determined by the test coil previously described. The set up is shown in the diagrammatic sketch given below. A represents the coil mounted on its movable carriage; B a Leeds and Northrup high sensitivity galvanometer No.PL3707 (figure of merit about 1 x 10^{-9}, resistance about 25 ohms); C a standard solenoid No.PL3351; D a secondary coil of 10 turns; and E a secondary of 1000 turns. R is a standard resistance. When determining ΔH the resistance R and the secondary E were shorted by an amalgamated copper link placed across gap 2, when determining H the link was placed across gap 1.

The method really consists in determining the number of lines per turn of unit area which will produce unit deflection of the galvanometer. Then by knowing the equivalent area of the test coil, the number of lines cut by it can be calculated if the corresponding galvanometer deflection is noted. The theory follows.



Let A_s be the equivalent area of the test coil; A_s' the equivalent area of the secondary, r the resistance of the circuit; k the ballistic sensibility of the galvanometer; and λ the logarithmic decrement. Now remembering that the quantity of electricity induced in a secondary circuit is given by the product of the effective area of the secondary times the number of lines cut, divided by the resistance of the circuit, we have

$$q = \frac{A_s \Delta H}{r}$$

as the quantity induced when the coil is moved, and this can be equated to $k(1+\lambda/2)d$ where d is the galvanometer deflection. Hence

$$\frac{A_s \Delta H}{r} = k(1+\lambda/2)d$$

or

$$k(1+\lambda/2)r = \frac{A_s \Delta H}{d}$$

Now confining our attention to the secondary coil. Whenever a current I' is made in the primary circuit a field H' is produced through the secondary and the galvanometer gives the deflection d'. It will be noted that the resistance of the secondary circuit is the same in this case as in the previous since the test coil and the secondary are in series. Therefore whenever the current I' is made or broken we can write

$$q = \frac{A_s' \ H'}{r} = k(1+\lambda/2)d'$$

whence

$$k(1+\lambda/2)r = \frac{A_s' \ H'}{d'}$$

Equating the two values of $k(1+\lambda/2)r$, we have

$$\frac{A_s \Delta H}{d} = \frac{A_s' \ H'}{d'}$$

$$\Delta H = \frac{A_s'}{A_s} \frac{H'}{d'} d$$

H' is equal to $\frac{4\pi N_p I'}{10L}$ where N_p is the number of turns and L is the total length of the standard solenoid, and I' the current.

$$\therefore \Delta H = \frac{A_s'}{As} \frac{4\pi N_p}{10L} \frac{I'}{d'} d$$

In case the test coil is thrown entirely out of the field then ΔH become H.

The constants are

A_s = 5.448 square centimeters

A_s' for ΔH = 10 x 13.56 = 135.6 square centimeters

A_s' for H = 1000 x 13.56 = 13560 square centimeters

$\frac{N_p}{L}$ = 6.14 turns per centimeter

$\frac{I'}{d'}$ depends upon the particular resistance used in the secondary circuit.

These figures give the constants

$$H = 192.42 \frac{I'}{d'} d$$

$$H = 19242 \frac{I'}{d'} d$$

In the determination of H the movable arm carrying the test coil was rotated through 180 degrees. Experiment showed that this procedure removed the coil to a point where the field was practically zero. The corresponding deflection of the galvanometer was recorded and the position of the carriage noted by reading the vernier. Δ H was determined by moving the carriage in the x-direction against a stop. The distance moved was generally 1 1/2 to 2 1/2 millimeters. The difference between the two positions of the carraige gave Δx. The position of the coil x'

for this value was taken as the mean of the two positions.

Curves between x and H and between x' and $\frac{\Delta H}{\Delta x}$ were run using magnetizing currents of 2.5, 5 and 10 amperes respectively. The object of this was to accurately locate the point where H $\frac{\Delta H}{\Delta x}$ is a maximum and also to ascertain whether or not this maximum shifted with the current. A number of curves for each value of the magnetizing current were run, these points all plotted on the same piece of coordinate paper and the best average curve drawn through them. From these curves value of H and $\frac{\Delta H}{\Delta x}$ were taken for various values of x and the product of corresponding values plotted against x. The result was a curve from which the position of the maximum could be found. A sample of the data is given.

A comparison of the curves show that the position of the maximum value of $H\frac{\Delta H}{\Delta x}$ falls in every case at the point x = 6.450 centimeters.

The position of this maximum was marked in the field as follows. A wooden try square cut off to the proper height was placed on the base of the electro magnet directly below the test coil when placed at the point of maximum. The position of the base of the try square was then marked with a scribe awl and a pin driven in the top of the square in such a manner that its head represented a point a trifle below that of the center of the test coil. By the use of such an arrangement it was always easy to put the sample in the position of the maximum.

Magnetizing Current 5 Amperes

Points Plotted Thus o

x in cm.	Δ x in cm.	x' in cm.	Δ H deflection	$\frac{\Delta H \text{ defl}}{\Delta x \text{ cm.}}$	$\frac{\Delta H \text{ lines}}{\Delta x \text{ cm.}}$	H deflection	H lines
9.145							
8.850	0.295	8.998	-2.92	-9.89	-465.7	8.00	4221
8.600	.250	8.725	-2.38	-9.52	-448.2	8.20	4326
8.310	.290	8.445	-2.50	-8.62	-405.9	8.43	4448
8.040	.270	8.175	-1.82	-6.74	-317.4	8.62	4548
7.820	.220	7.930	-0.82	-3.73	-175.6	8.70	4590
7.620	.200	7.720	-0.11	-0.55	- 25.9	8.70	4590
7.395	.225	7.508	+0.86	+3.82	179.9	8.64	4559
7.195	.200	7.295	1.62	8.10	381.4	8.46	4464
6.990	.205	7.093	2.63	12.83	604.1	8.20	4326
6.705	.285	6.848	4.70	16.49	776.4	7.80	4115
6.550	.155	6.628	2.96	19.10	899.3	7.52	3968
6.320	.230	6.435	4.60	20.00	941.7	7.09	3741
6.140	.180	6.230	3.72	20.67	973.2	6.78	3577
5.955	.185	6.048	3.82	20.65	972.3	6.40	3377
5.730	.225	5.843	4.48	19.91	937.5	6.00	3166
5.510	.220	5.620	4.10	18.64	877.7	5.65	2981
5.255	.255	5.383	4.43	17.37	817.9	5.23	2759
5.070	.180	5.165	3.04	16.89	795.3	4.94	2606
42.00							
39.90	.210	4.095	2.43	11.57	544.8	3.72	1963

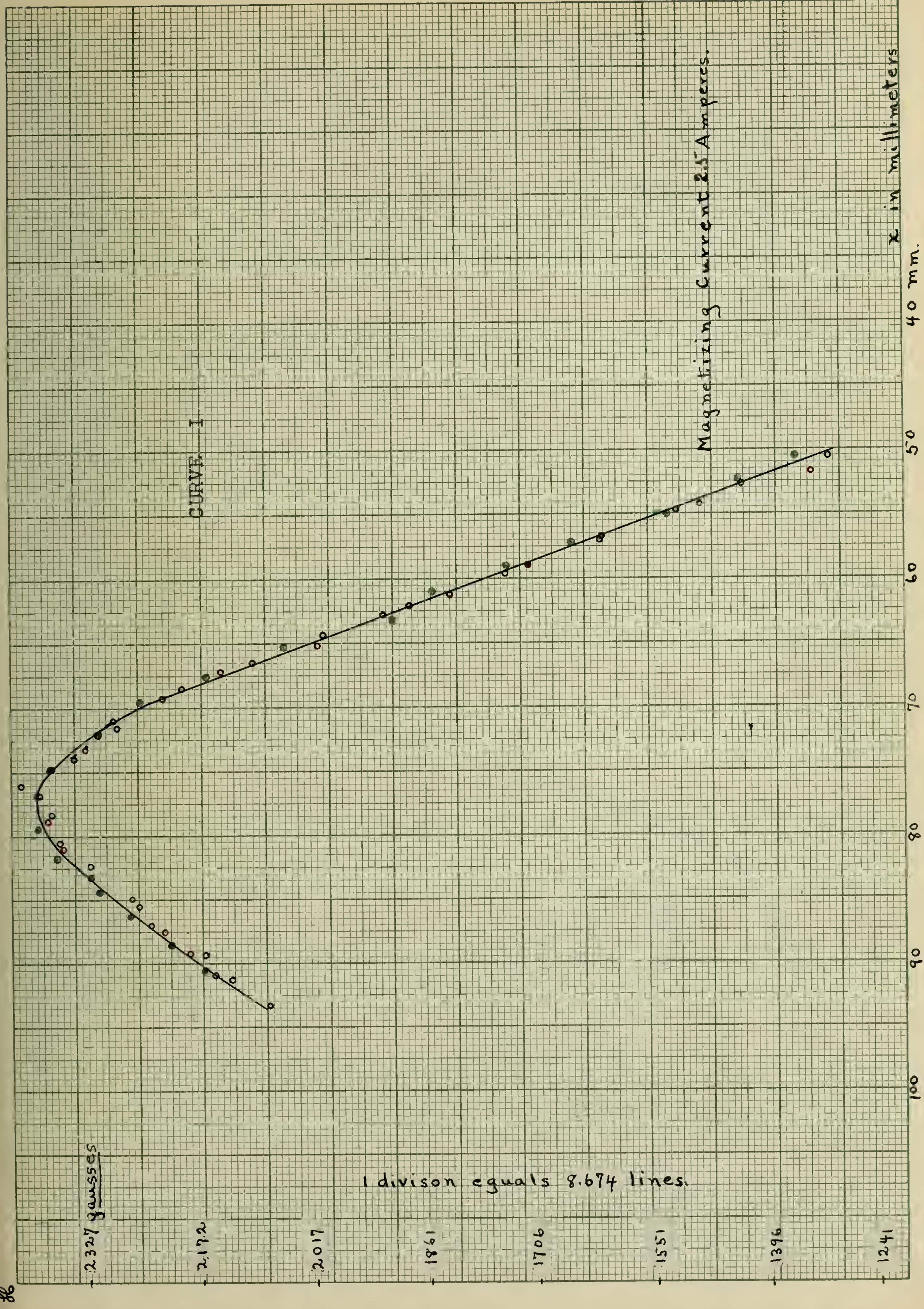
$\frac{I'}{d'} = 0.2447$ for Δ H   H = 47.085d

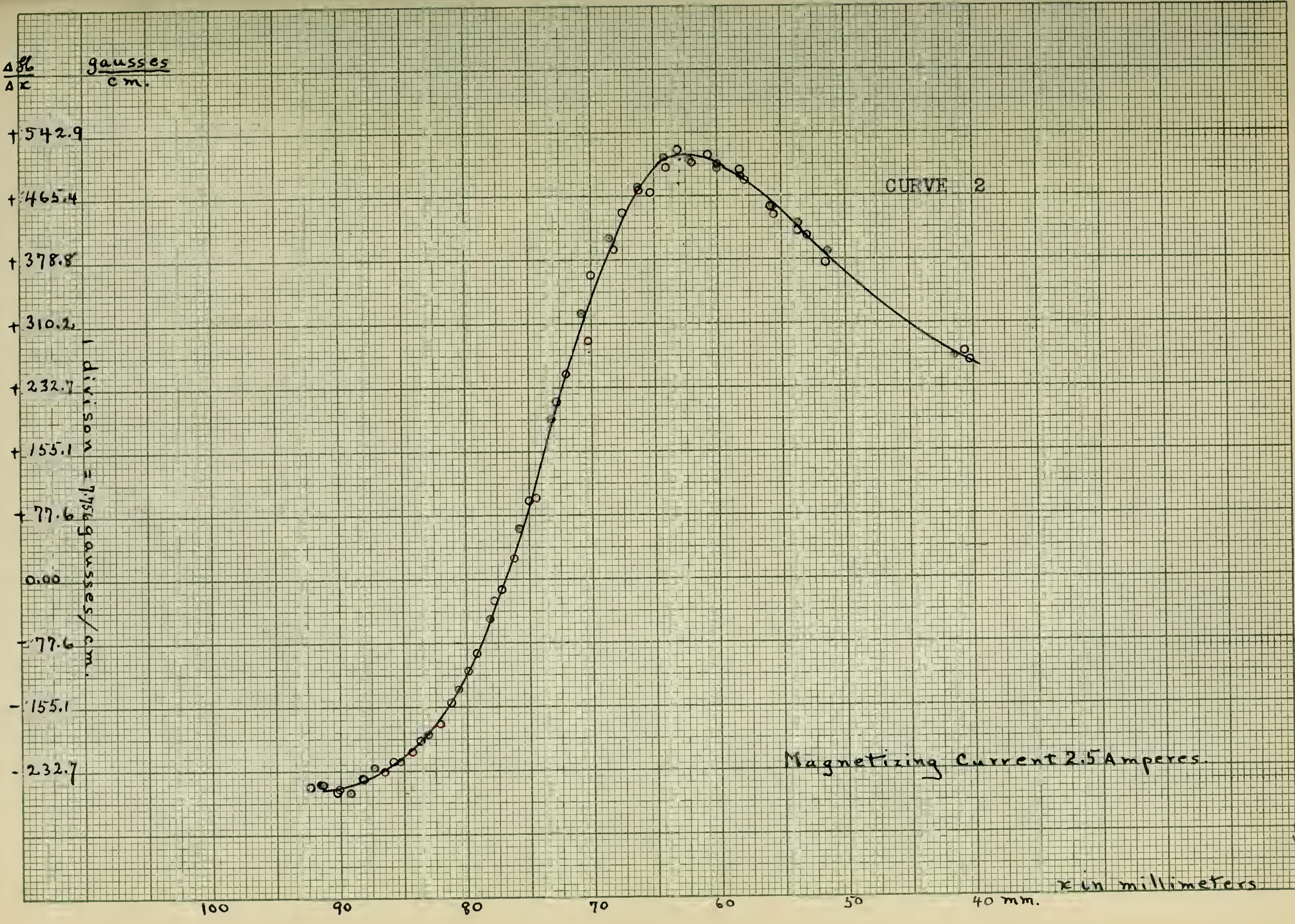
$\frac{I'}{d'} = 0.02742$ for H.   H = 527.62d

Data for $H\frac{\Delta H}{\Delta x}$ Curve

(Taken from Curves 4 and 5)

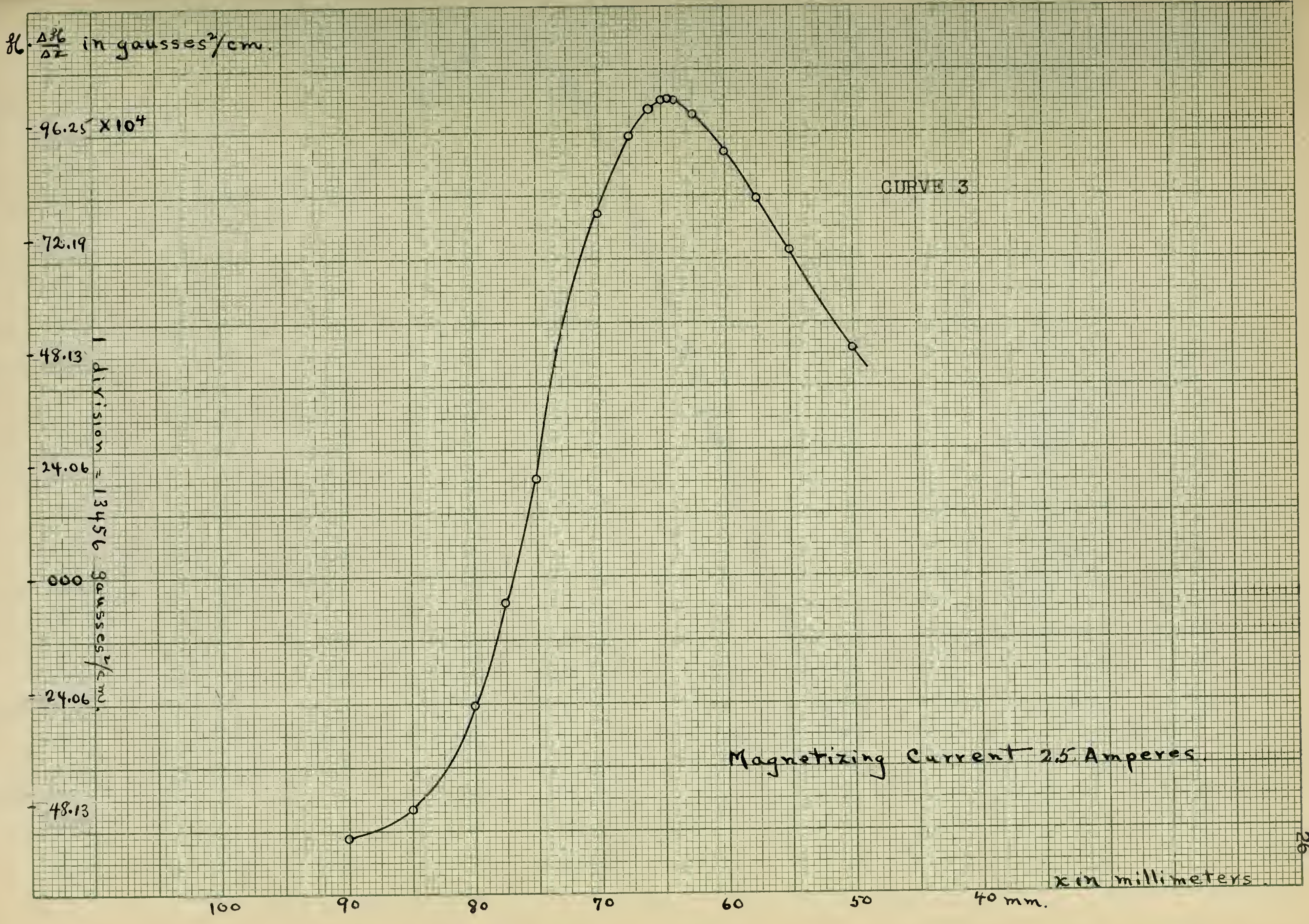
x	H	$\frac{\Delta H}{\Delta x}$	$H\frac{\Delta H}{\Delta x}$
90	4112	-480.9	-1977 x 10^3
85	4398	-417.3	-1835
80	4559	-235.8	-1075
77.5	4589	- 58.9	-270
75	4564	+181.5	+828
70	4356	690.3	3007
67.5	4146	837.7	3473
66	3999	899.7	3598
65	3900	933.8	3642
64.5	3860	949.3	3665
64	3808	961.8	3662
62.5	3660	977.3	3577
60	3420	960.2	3283
57.5	3190	912.1	2910
55	2958	860.9	2547
50	2583	749.2	1935


CURVE I
Magnetizing Current 2.5 Amperes.
x in millimeters
40 mm.
50
60
70
80
90
100
1 divison equals 8.674 lines.
gausses
2327
2172
2017
1861
1706
1551
1396
1241
ℬ



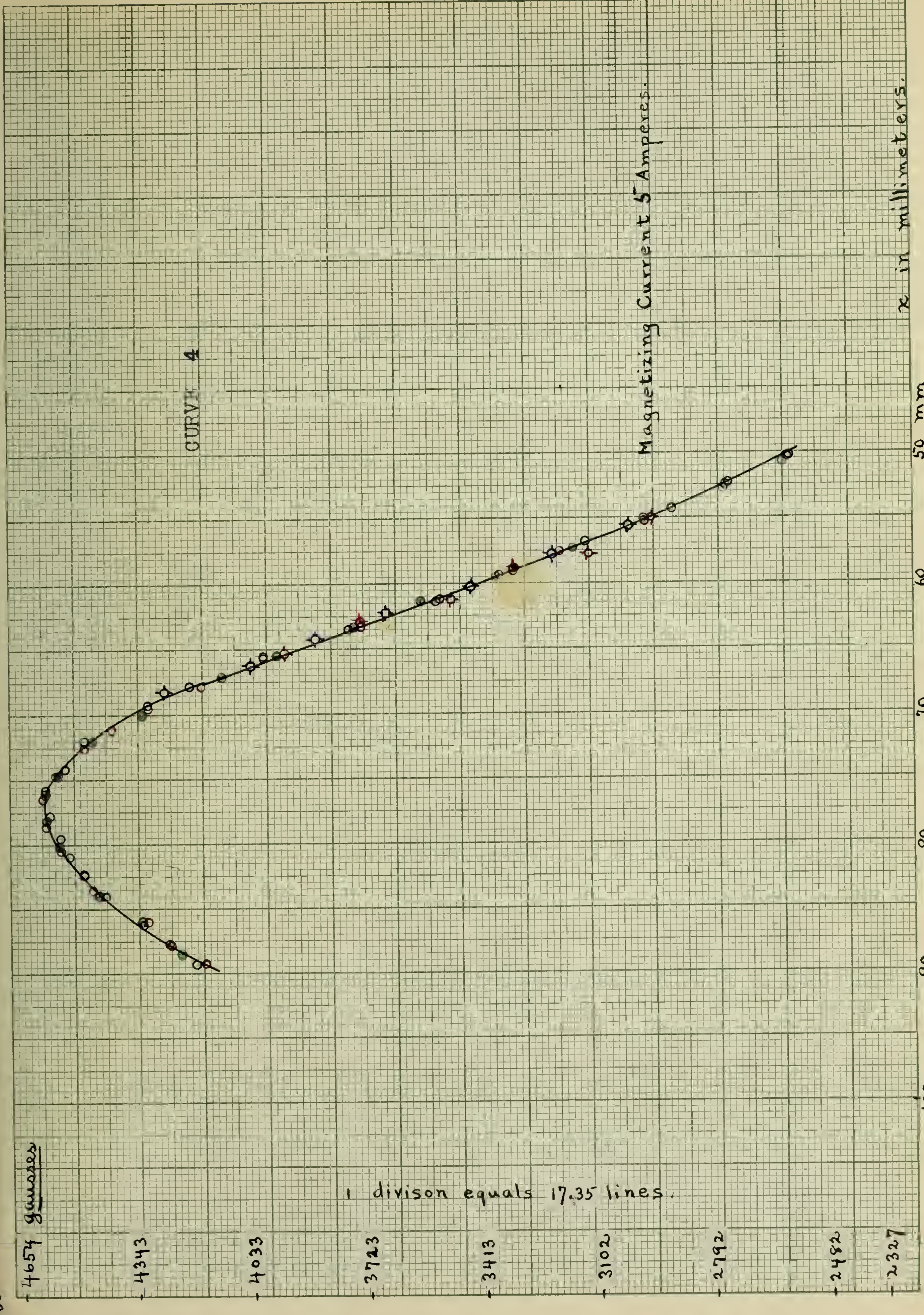
CURVE 2

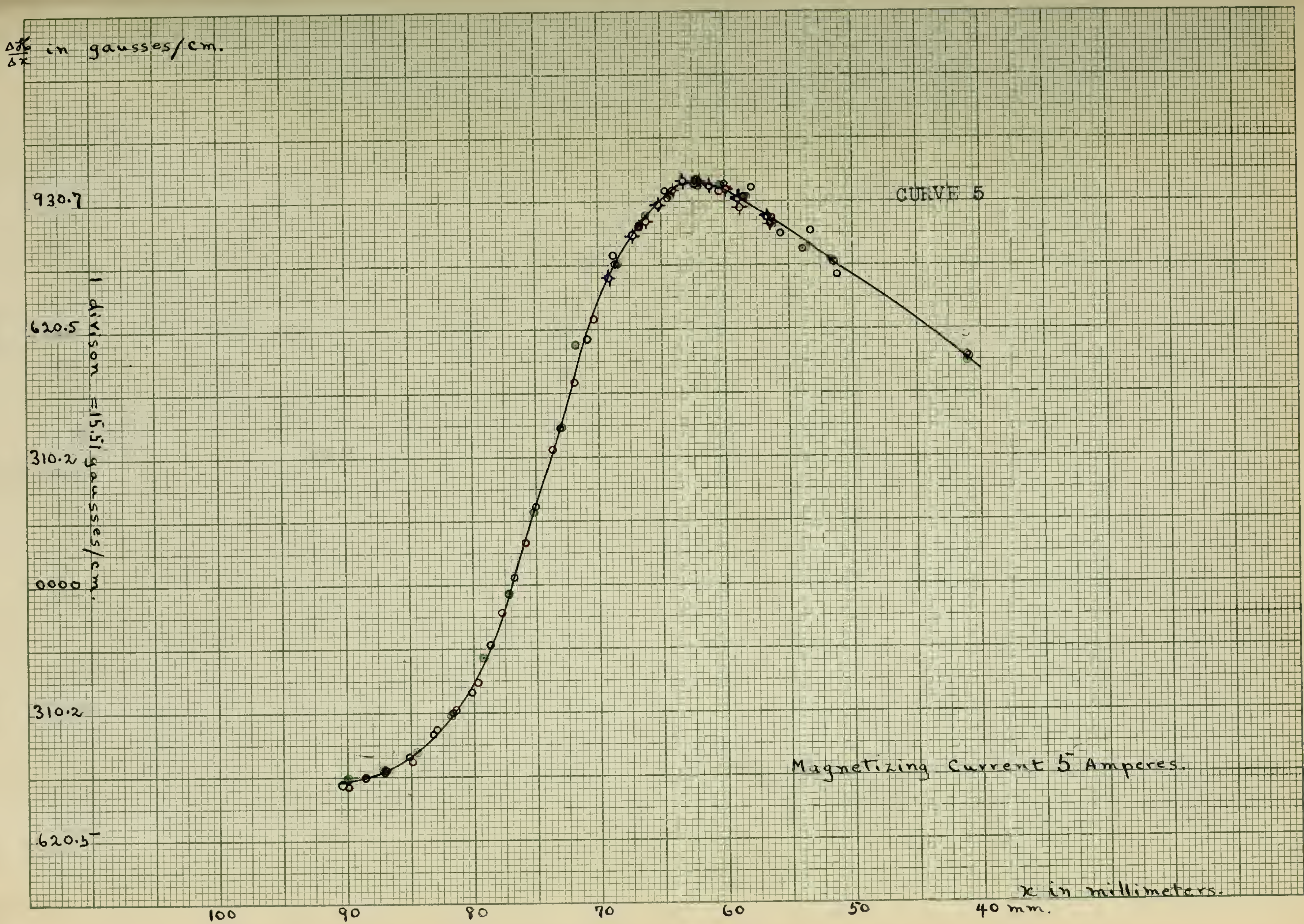
Magnetizing Current 2.5 Amperes.

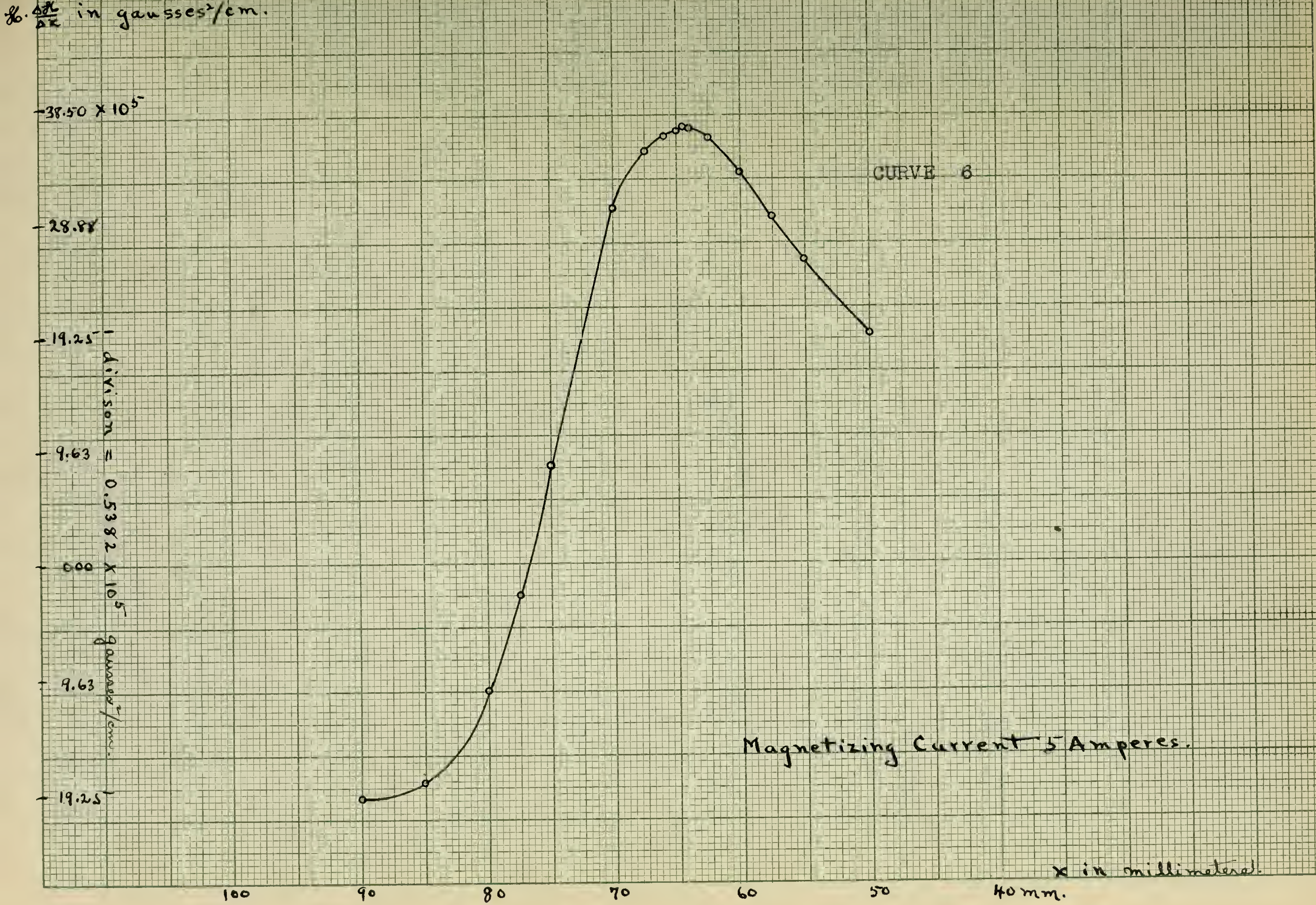


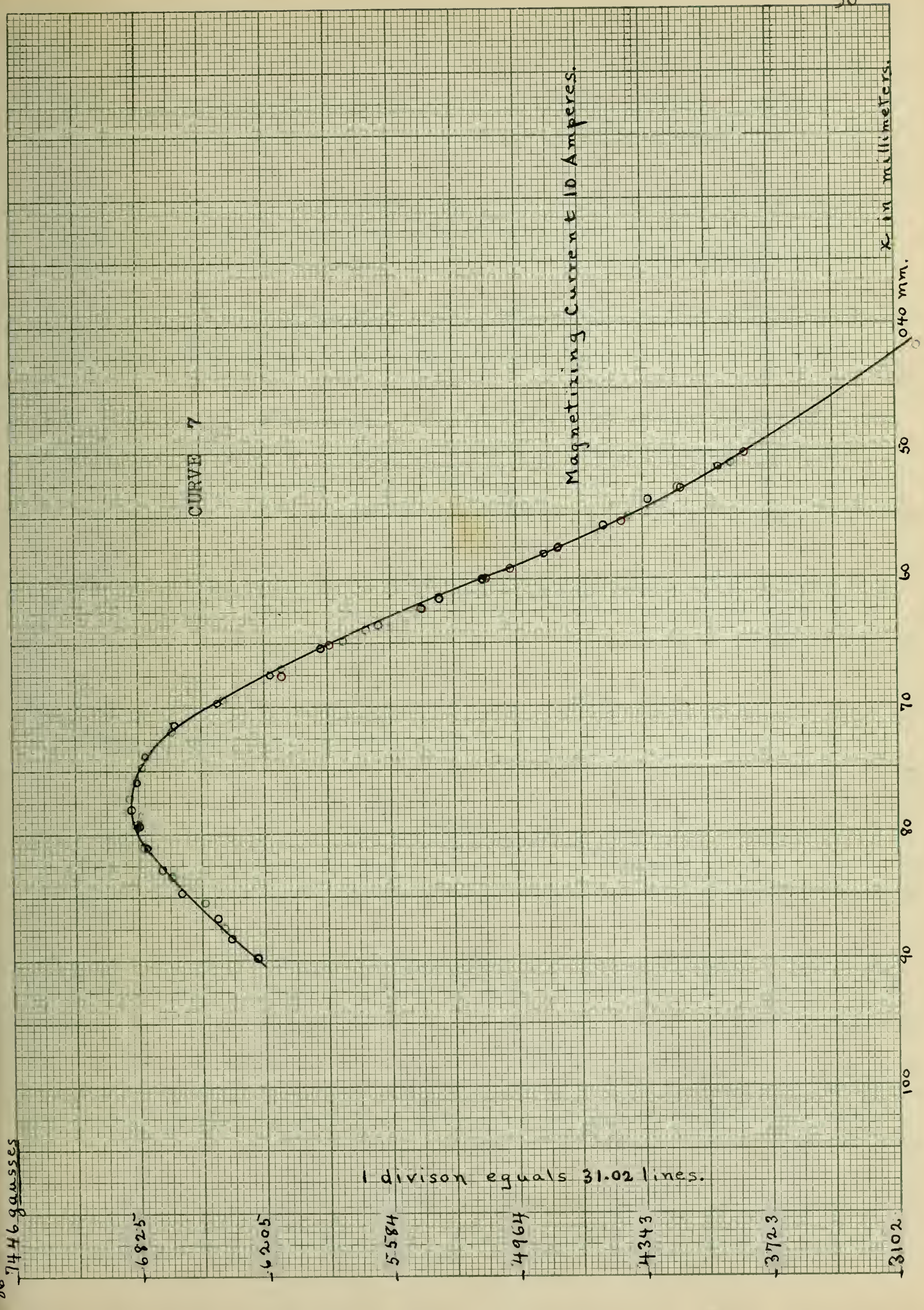
CURVE 3

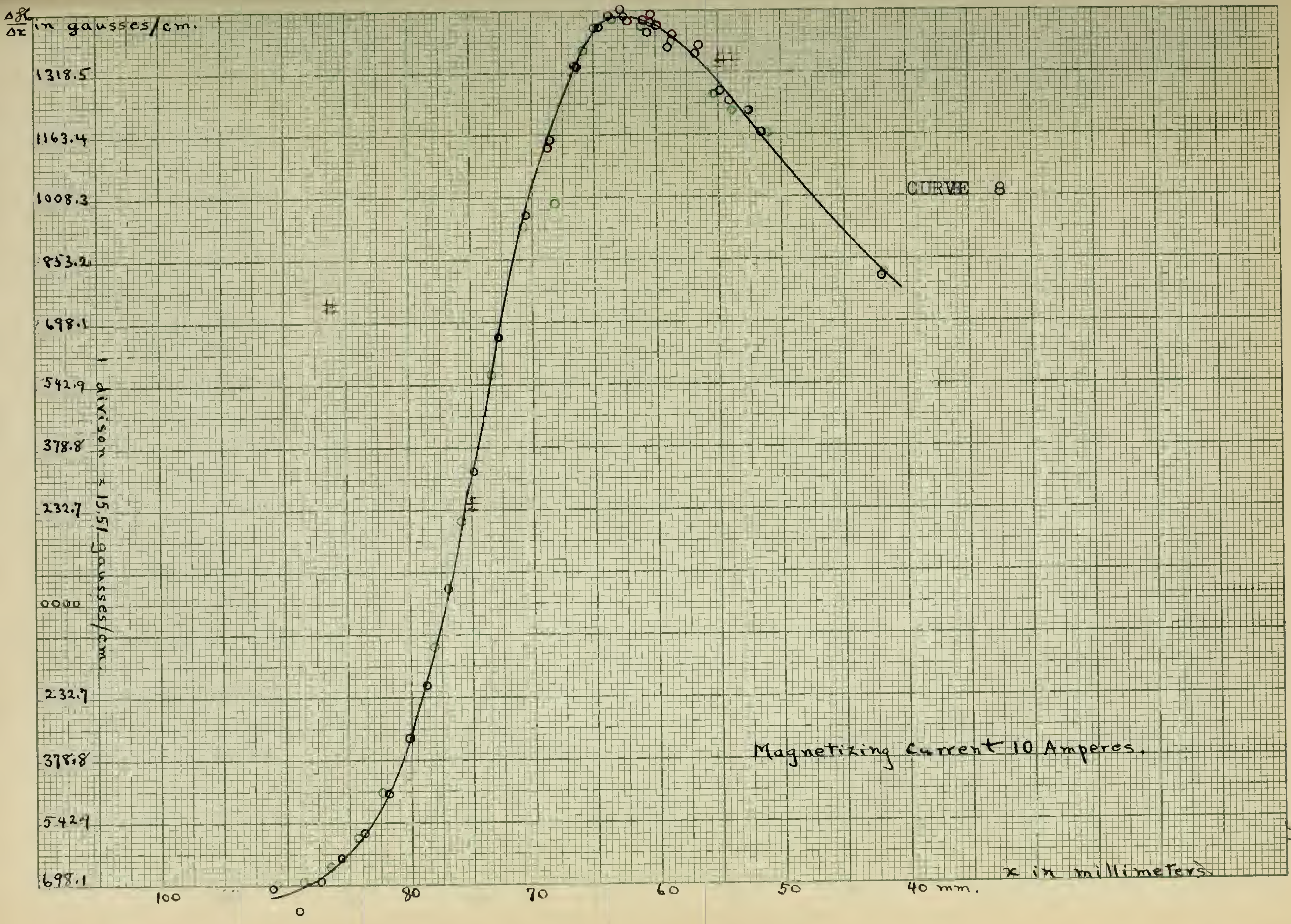
$\mathcal{H} \cdot \frac{\Delta \mathcal{H}}{\Delta x}$ in gausses²/cm.
96.25 X 10⁴
72.19
48.13
24.06
000
24.06
48.13
1 division = 13456 gausses²/cm.
Magnetizing Current 2.5 Amperes.
x in millimeters.
100
90
80
70
60
50
40 mm.

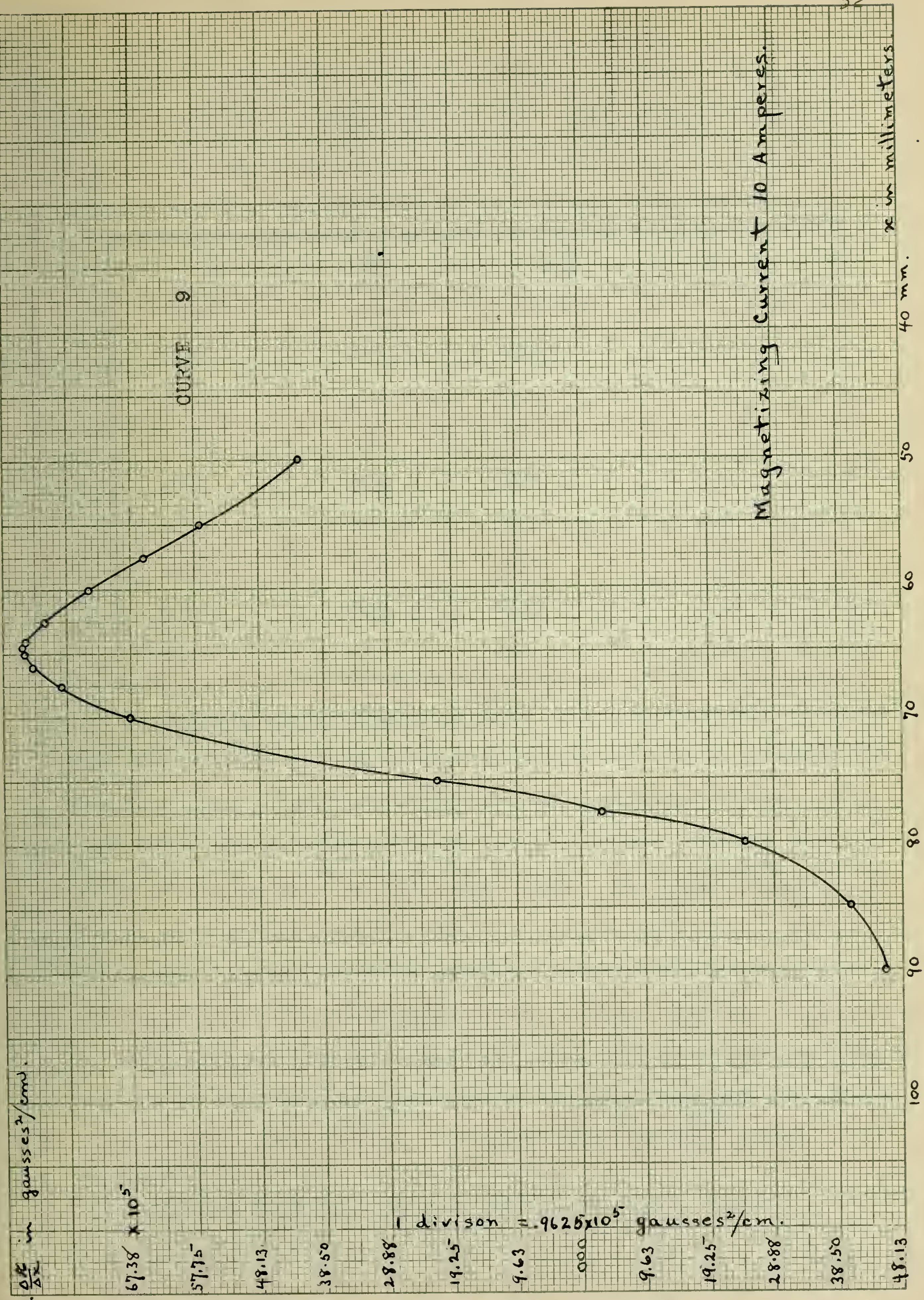

CURVE 4
Magnetizing Current 5 Amperes.
x in millimeters.
50 mm
60
70
80
90
100
Gausses
4654
4343
4033
3723
3413
3102
2792
2482
2327
1 divison equals 17.35 lines.


$\frac{\Delta H}{\Delta x}$ in gausses/cm.
CURVE 5
930.7
620.5
310.2
0000
310.2
620.5
1 divison =15.51 gausses/cm.
Magnetizing Current 5 Amperes.
x in millimeters.
100
90
80
70
60
50
40 mm.


$\mathcal{H} \cdot \frac{\Delta \mathcal{H}}{\Delta x}$ in gausses²/cm.
-38.50 × 10⁵
-28.88
-19.25
-9.63
0.00
9.63
19.25
1 divison = 0.5382 × 10⁵ gausses²/cm.
CURVE 6
Magnetizing Current 5 Amperes.
x in millimeters.
100
90
80
70
60
50
40 mm.


CURVE 7
Magnetizing Current 10 Amperes.
x in millimeters.
040 mm.
50
60
70
80
90
100
1 divison equals 31.02 lines.
7446 gausses
6825
6205
5584
4964
4343
3723
3102


$\frac{\Delta H}{\Delta x}$ in gausses/cm.
1318.5
1163.4
1008.3
853.2
698.1
542.9
378.8
232.7
0000
232.7
378.8
542.9
698.1
1 divison = 15.51 gausses/cm.
CURVE 8
Magnetizing Current 10 Amperes.
x in millimeters.
100
0
80
70
60
50
40 mm.


CURVE 9
Magnetizing Current 10 Amperes.
ℋ · ΔH/Δx in gausses²/cm.
67.38 x 10⁵
57.75
48.13
38.50
28.88
19.25
9.63
000
9.63
19.25
28.88
38.50
48.13
1 divison = .9625x10⁵ gausses²/cm.
40 mm.
50
60
70
80
90
100
x in millimeters

After the position of the maximum had been found, the values of H, $\frac{\Delta H}{\Delta x}$ and $H\frac{\Delta H}{\Delta x}$ was found for various magnetizing currents. Five determinations at least were taken for each measurement and the values given below represent the averages.

H	$\frac{\Delta H}{\Delta x}$	$H\frac{\Delta H}{\Delta x}$	I
804.4	193.3	155.5 x 10^3	1.0 ampere
1192	290.0	345.7 "	1.5
1590	378.3	602 "	2.0
1986	484	962 "	2.5
2383	580	1382 "	3.0
3148	777.5	2448 "	4.0
3881	946	3672 "	5.0
5062	1242	6286 "	7.5
5761	1425	8211 "	10.0

Calibration of Thermocouple:- For temperatures above 0°C the thermocouple was calibrated by comparing with a standard thermometer. For points below zero the melting point of mercury (-38.9°C), the melting point of toluol (-102°C) and the boiling point of liquid air (-191°C) were taken. The temperature of the liquid air was ascertained from its specific gravity.* The possible error in the specific gravity measurement indicates that the temperature of the liquid air lay between -189.8°C and -191.5°C. It was observed, however, that the deflection given by the galvanometer in the thermocouple circuit depended upon the amount the thermocouple was submerged. This was no doubt due to the

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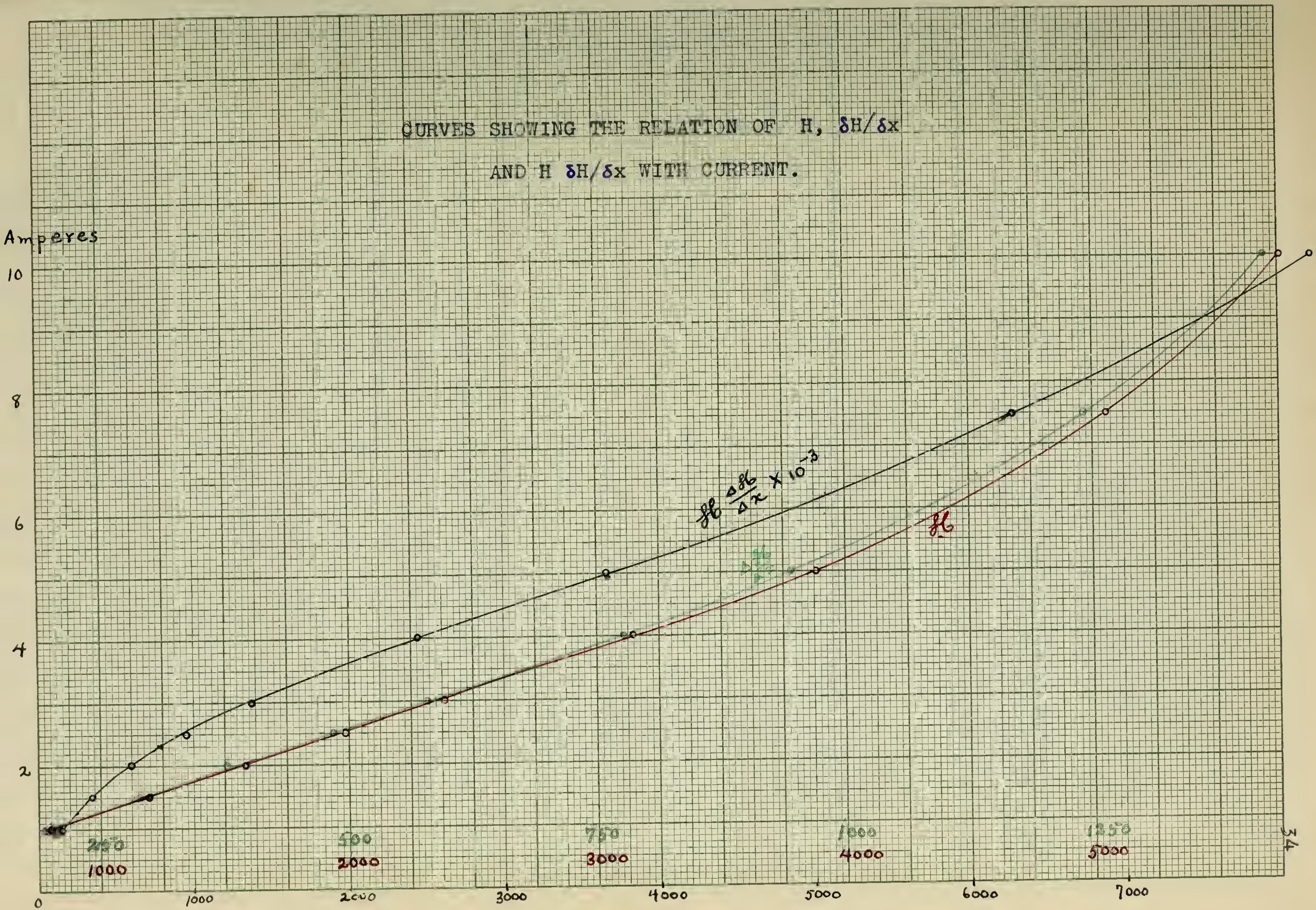
* Behn and Kiebitz: Ann. d. Physik. 12, 421, (1903)



CURVES SHOWING THE RELATION OF H, δH/δx

AND H δH/δx WITH CURRENT.

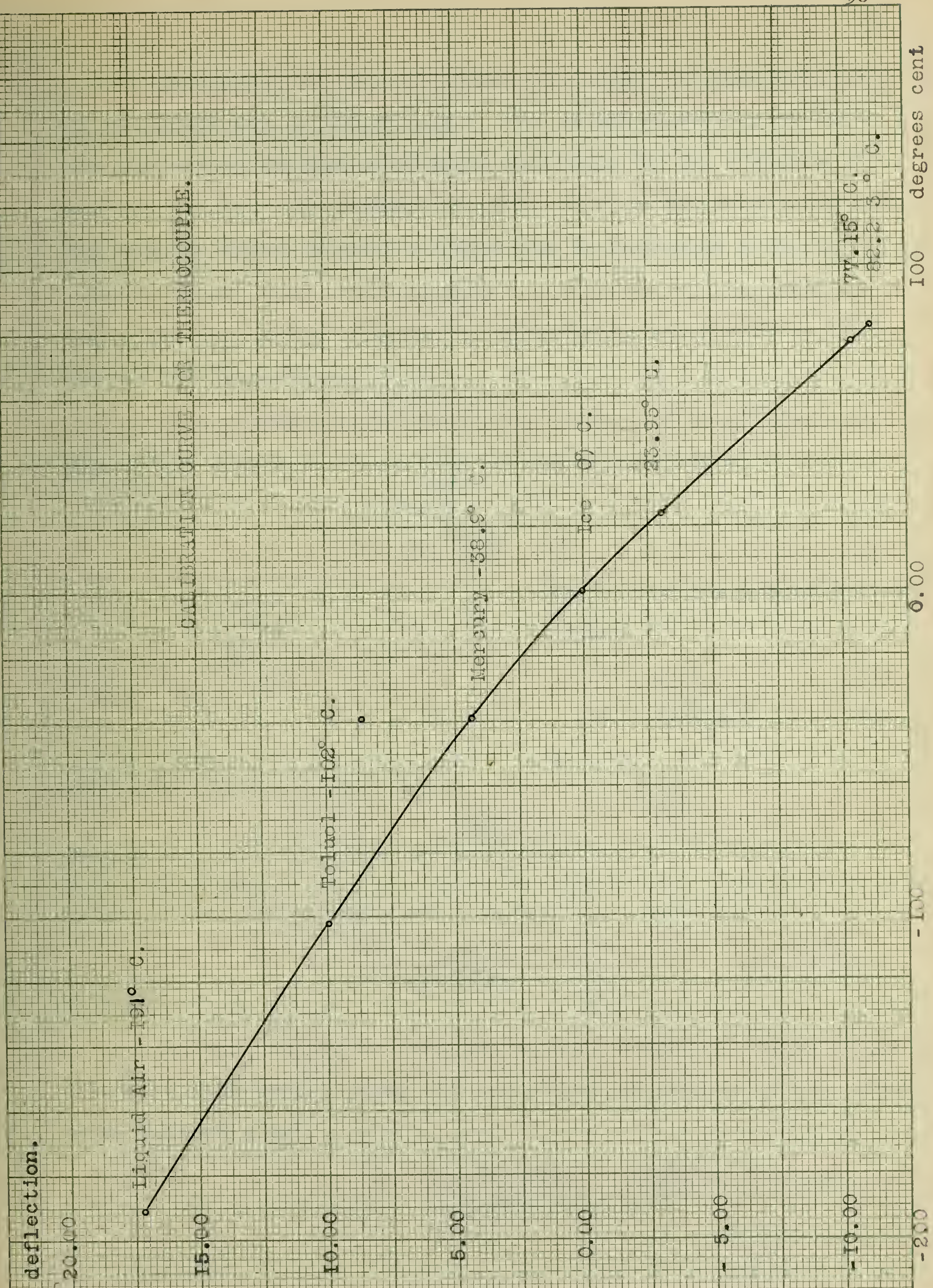
composition of the liquid air changing as we dip down beneath the surface.

The constant temperature junction of the couple was kept in a bath of shaved ice and water; the bath always containing more ice than water. The toluol and mercury points were obtained by pouring small lumps of the frozen material into a small amount of liquid and stirring the mixture as vigorously as possible with the thermocouple.

Calibration Data

Substance	Temperature	Deflection
Liquid air (boiling)	-191°C	17.14 cm.
Toluol (melting)	-102°	9.90
Mercury (melting)	-38.9°	4.305
Ice (melting)	0.00	0.00
Water	23.95	-3.06
Water	77.15	-10.37
Water	82.23	-11.12

In every case the deflection was obtained by reading the galvanometer with the couple direct and reversed and dividing the resulting difference by two.

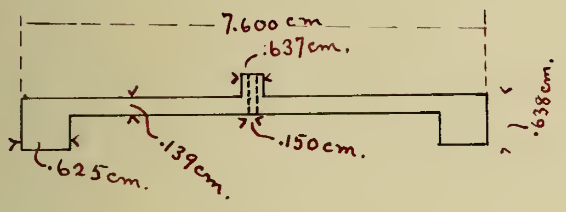

CALIBRATION CURVE FOR THERMOCOUPLE.
deflection.
20.00
15.00
10.00
5.00
0.00
- 5.00
-10.00
-200
- 100
0.00
100
degrees cent
Liquid Air -191° C.
Toluol -102° C.
Mercury -38.9° C.
Ice 0° C.
25.95° C.
77.15° C.
82.23° C.

Determination of Coefficient of Torsion of Suspension and of the Lever Arm of the Sample:- The couple necessary to twist the suspension through unit angle was found by the ordinary vibration method. The period "t" of the system was determined with the damping vanes removed but with the thermocouple wires in place. Then a disc of known moment of inertia was suspended at the point ordinarily occupied by the damping vanes and the new period "t'" determined.

If I represents the moment of inertia of the first system and I' the moment of inertia of the added disc, then

$$t = 2\pi\sqrt{\frac{I}{C}} \qquad (1)$$

$$t' = 2\pi\sqrt{\frac{I+I'}{C}} \qquad (2)$$



Brass Moment of Inertia Disc

where C is the couple desired.

Squaring

$$t^2 = 4\pi^2\frac{I}{C} \qquad (3)$$

$$t'^{8} = 4\pi^2\frac{I+I'}{C} \qquad (4)$$

From (3)

$$I = \frac{t^2C}{4\pi^2}$$

Whence

$$t'^2 = 4\pi^2\frac{\frac{t^2C}{4\pi^2} + I'}{C}$$

$$Ct'^2 = t^2C + 4\pi^2I'$$

$$C = \frac{4\pi^2I'}{(t'^2-t^2)}$$

In our particular case the periods t and t' were 8.11 and 11.01 seconds respectively and the moment of inertia of the added disk 1084.76 g cm^2.

$$C = \frac{4 \times (3.1416)^2 \times 1084.76}{(11.01)^2 - (8.11)^2} = 772.34\text{dyne/cm.}$$

The lever arm of the capsule containing the sample was 10.45 centimeters. It was determined using an improvised cathetometer. A telescope carrying cross hairs was mounted on a slip ring so as to be free to move in a horizontal direction and to turn on a horizontal axis. The cross hairs were first sighted on the suspension and the position of the slip ring marked on the rod. The cross hairs were next sighted on the capsul and this position marked. The distance between the two marks is the distance desired.

V OBSERVATIONS

The oxides of six of the rare earths were investigated; namely, the oxides of Neodymium (Nd_2O_3), Ytterbium (Yb_2O_3), Erbium (Er_2O_3), Gadolinium (Gd_2O_3), Holmium (Ho_2O_3) and Dysprosium (Dy_2O_3). All the above materials were obtained from Dr. Balke of the Chemistry Department, University of Illinois, and with the exception of the Holmium, were of high purity.

The manipulation consisted in weighing the capsule after it had been carefully cleaned, introducing the sample and weighing again. The difference between the two weights represented the amount of the material used. The capsule was then secured to the arm of the torsion balance and the thermocouple lowered so that the junction was well surrounded by the sample. The thermocouple was left in the capsule throughout the entire set of measurements as previous experiments showed that its presence did not influence the final value determined for the susceptibility.

The capsule was next placed in the hollow of the heavy copper rod used for obtaining the low temperatures and a piece of paper was wrapped around the rod connecting it with glass tube surrounding the vertical portion of the aluminum rod. This placed the entire torsion system in a closed space and eliminated trouble due to air currents, etc.

Before adding the liquid air, two or three measurements of the susceptibility were made at room temperature and the mean taken as the true value. Then the liquid air was added, generally in small amounts, and the susceptibility measured for the lower temperatures. The temperature was determined by reading the thermocouple galvanometer just before, at the same time and just after the

susceptibility measurement, reversing the galvanometer after each reading. The set in the suspension of the torsion balance was allowed for by taking a zero reading just before and just after applying the current to the electromagnet. The mean of the two zero readings was assumed to be the true zero.

The total deflection or twist on the suspension when a sample was in the capsule was due partially to the sample and partially to the material composing the capsule. The portion due to the sample was found by subtracting from the total an amount found by making a blank test on the empty capsule under similar conditions.

Before using any of the oxides of the rare earths, they were blasted at a temperature of about 1000°C in a platinum crucible. This served to drive off all moisture and to decompose any carbonate which may have formed.

A detailed set of data on erbium oxide is given below. It will serve as an illustration of the way in which the data were collected. Thereafter only the results will be given.

Erbium Oxide (Er_2O_3)

Sample No. 1

Purity about 95% Contains 3 - 5% yttrium

and possibly a trace of thulium.

weight of capsule			weight of capsule and sample		
8	14		2	12	
8	12	1.10550	2	11	1.15286
6	13		1	12	
7	7		2	2	
	16			10	
	3			5	

1.15286
1.10550
0.04736 g. = weight of sample

Magnetizing current used 1.5 amperes

Thermocouple			Torsion Balance		
direct	reversed	deflection	zero	reading	deflection
22.00 22.02	27.86	-2.93	25.30 25.30	18.00	7.30
22.08	27.80 27.80	-2.86	25.30 25.26	18.00	7.28
24.73 25.10	24.92	0.00	25.32 25.30	17.54	7.77
26.78 27.02	23.00	1.95	25.30 25.28	16.91	8.38
28.35	21.58 21.44	3.42	25.30 25.26	16.60	8.68
29.92 30.30	19.80	5.15	25.30 25.30	15.91	9.39
32.32	17.92 17.46	7.31	25.30 25.26	14.92	10.36
33.66 33.80	16.22	8.76	25.26 25.22	14.24	11.00
34.80 34.90	15.22	9.81	25.22 25.24	13.52	11.71
36.20 36.46	13.72	11.29	25.30 25.24	12.04	13.23
37.88	12.31 12.20	12.81	25.24 25.24	10.00	15.24
38.68 38.70	11.42	14.63	24.90 24.60	8.80?	15.95?

Correction for capsule .55 for all temperatures.

$10^6 \cdot \chi$ = 21.62 times the corrected deflection. This is calculated as follows:

From page 6 we have

$$\chi = \frac{1}{M\, H\frac{\partial H_y}{\partial x}} \cdot \frac{c\,\varphi}{l} . \qquad M = 0.04736g. \qquad H_y \frac{\partial H_y}{\partial x} = 345.7 \times 10^3$$

for a magnetizing current of 1 1/2 amperes (page 33),

c = 772.34 dyne cm. (page 37), l = 10.4 cm. (page 38)

φ = the deflection divided by twice the scale distance (2 x 104.4 cm. (page 15).

$$\chi = \frac{772.34}{0.04736 \times 345.7 \times 10^3 \times 10.45 \times 2 \times 104.4}\, d$$

or

$$\chi = 21.62\, d \cdot 10^{-6} \text{ per unit mass.}$$

The susceptibilities then for this particular case are obtained by multiplying the corrected deflection of the torsion balance, i.e., deflection minus 0.55, by 21.62 x 10^{-6}. The temperatures were determined by reference to a calibration curve plotted to a large scale. The results are given below.

Points Plotted Thus o

Thermocouple deflection	Temperature °C	Torsion balance deflection	Corrected deflection	$\chi \cdot 10^6$
-2.93	23	7.30	6.75	145.9
-2.86	22.5	7.28	6.73	145.5
0.00	0.00	7.77	7.22	156.1
1.95	-16	8.38	7.83	169.3
3.42	-30	8.68	8.13	175.8
5.15	-48.5	9.39	8.84	191.1

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Continued

Thermocouple deflection	Temperature °C	Torsion balance deflection	Corrected deflection	$\chi \cdot 10^6$
7.31	-70.6	10.36	9.81	212.1
8.76	-87.5	11.00	10.45	225.9
9.81	-100.4	11.71	11.16	241.3
11.29	-118.6	13.23	12.68	274.1
12.81	-138.2	15.24	14.69	317.6
14.63	-161.2	15.95?	15.40?	332.9?

Sample No.2

Points plotted thus ○ Weight of sample 0.05688 g.

Correction 0.55 $10^6 \cdot \chi = 18.00\ d$

Thermocouple deflection	Temperature °C	Torsion balance deflection	Corrected deflection	$\chi \cdot 10^6$
-3.14	25.	8.58	8.03	144.5
-1.92	16.	8.84	8.29	149.2
-0.29	2.5	9.27	8.72	157.0
2.20	-19.	9.97	9.42	169.6
5.13	-48.	11.22	10.67	192.1
6.80	-65.5	12.06	11.51	207.2
7.56	-74.	12.53	11.98	215.6
9.95	-102.	14.10	13.55	243.9
11.95	-127.5	16.68	16.13	290.3
13.88	-152.	20.08	19.53	351.5

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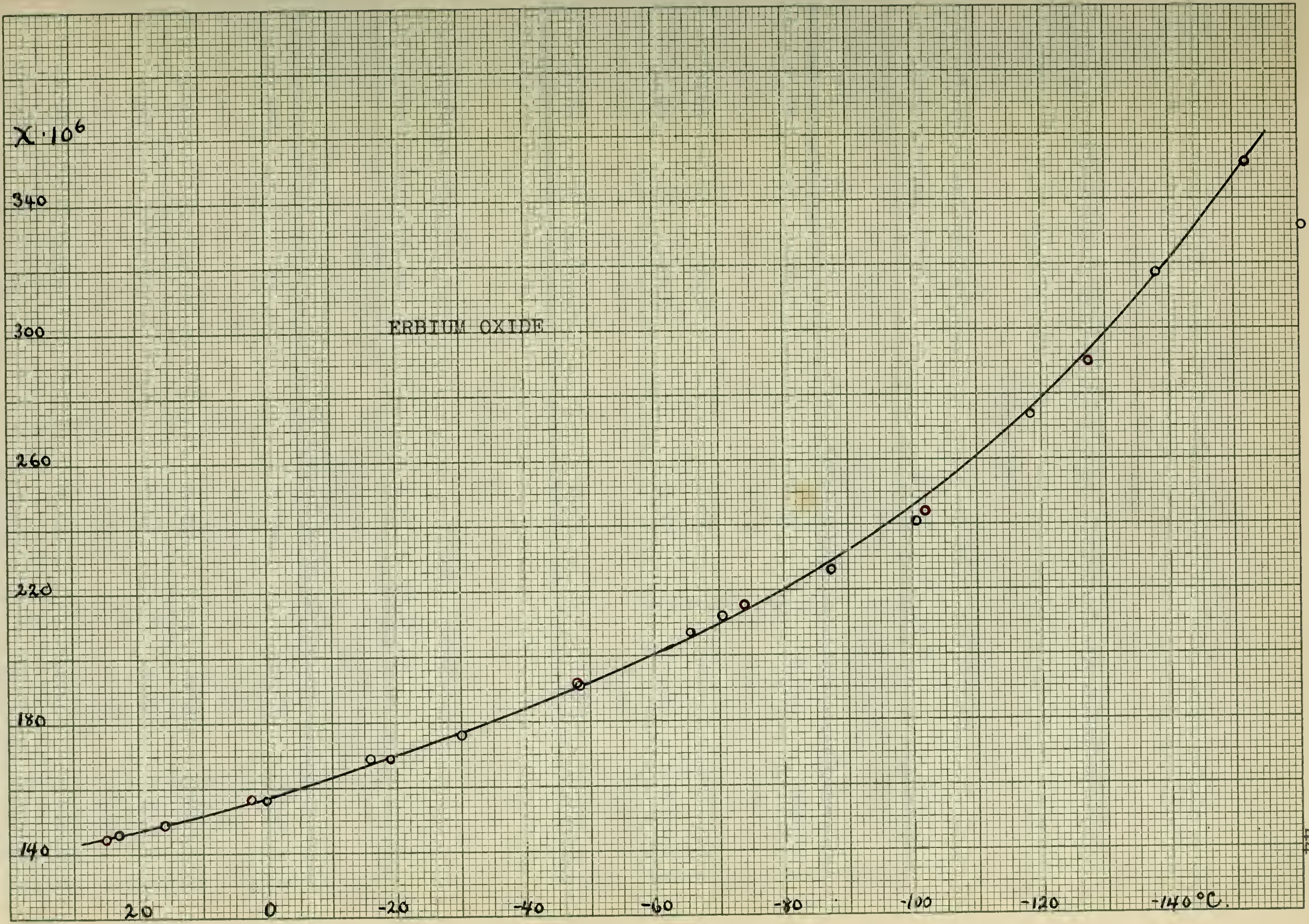
ERBIUM OXIDE
X·10⁶
340
300
260
220
180
140
20
0
-20
-40
-60
-80
-100
-120
-140°C.

Dysprosium Oxide (Dy_2O_3)

Practically free from Holmium

Contains traces of Terbium, Neodymium and Praseodymium

Sample No. 1

Points plotted thus o Weight 0.01675 g.

Correction -0.55 $\chi \cdot 10^6 = 61.13\ d$

Thermocouple deflection	Temperature °C	Torsion balance deflection	Corrected deflection	$\chi \cdot 10^6$
-3.07	24.	4.29	3.74	228.6
+2.92	-25.5	5.16	4.61	281.8
5.56	-52.5	5.62	5.07	309.9
7.69	-75.5	6.01	5.46	337.7
10.57	-109.5	7.17	6.62	404.7
12.60	-135.5	8.29	7.74	473.1

Sample No. 2

Points plotted thus o Weight 0.0280 g.

Correction -0.55 $\chi \cdot 10^6 = 36.57\ d$

Thermocouple deflection	Temperature °C	Torsion balance deflection	Corrected deflection	$\chi \cdot 10^6$
-3.44	27.	6.74	6.19	226.4
+1.34	-11	7.54	6.99	255.6
4.35	-41	8.30	7.75	283.4
6.68	-65	9.10	8.55	312.7
8.16	-81	9.78	9.23	337.5
11.75	-125	12.58	12.03	439.9
12.93	-140	13.45	12.90	471.8

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Sample No. 3

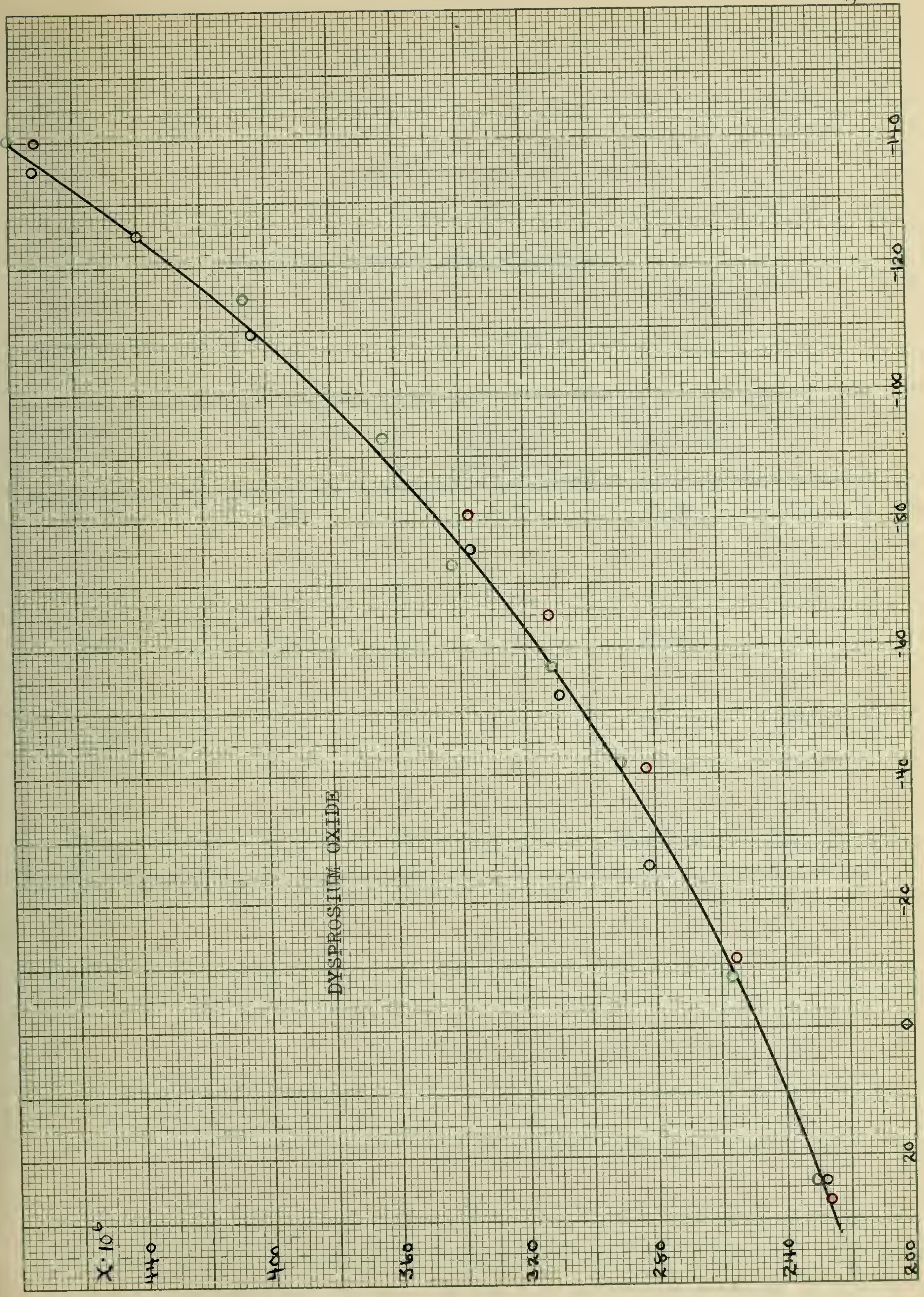
Points plotted thus o

Weight 0.03780 g.

Correction -0.55

$\chi \cdot 10^6 =$ 27.09 d

Thermocouple deflection	Temperature °C	Torsion balance deflection	Corrected deflection	$\chi \cdot 10^6$
-3.08	24	9.09	8.54	231.3
+0.93	- 8	10.10	9.55	258.7
4.31	-42	11.27	10.72	290.4
6.01	-57	12.08	11.53	312.3
7.50	-73	13.22	12.67	343.2
9.24	-93	14.00	13.45	364.4
11.03	-115	15.38	15.03	407.2
13.00	-140.5	18.30	17.75	480.8


DYSPROSIUM OXIDE
X·10^6
440
400
360
320
280
240
200
-140
-120
-100
-80
-60
-40
-20
0
20

Gadolinium Oxide (Gd_2O_3)

about 97%

Contains Bismuth and Magnesium

Magnetizing Current 1 1/2 amperes Weight 0.05446 g.

Correction -0.55 $\chi \cdot 10^6$ = 18.80 d.

Thermocouple deflection	Temperature °C	Torsion balance deflection	Corrected deflection	$\chi \cdot 10^6$
-3.24	27	9.03	8.48	159.4
+0.22	- 2	9.96	9.41	176.9
1.87	-16	10.44	9.89	185.9
4.35	-41	11.46	10.91	205.1
8.63	-86	14.02	13.47	253.2
10.52	-109	15.67	15.12	284.3
11.57	-122	16.95	16.40	308.3
13.86	-151	20.94	20.39	383.3
13.73	-149	20.65	20.10	377.9

[illegible]

[illegible]

[illegible]

[illegible]

[illegible]

[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
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[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
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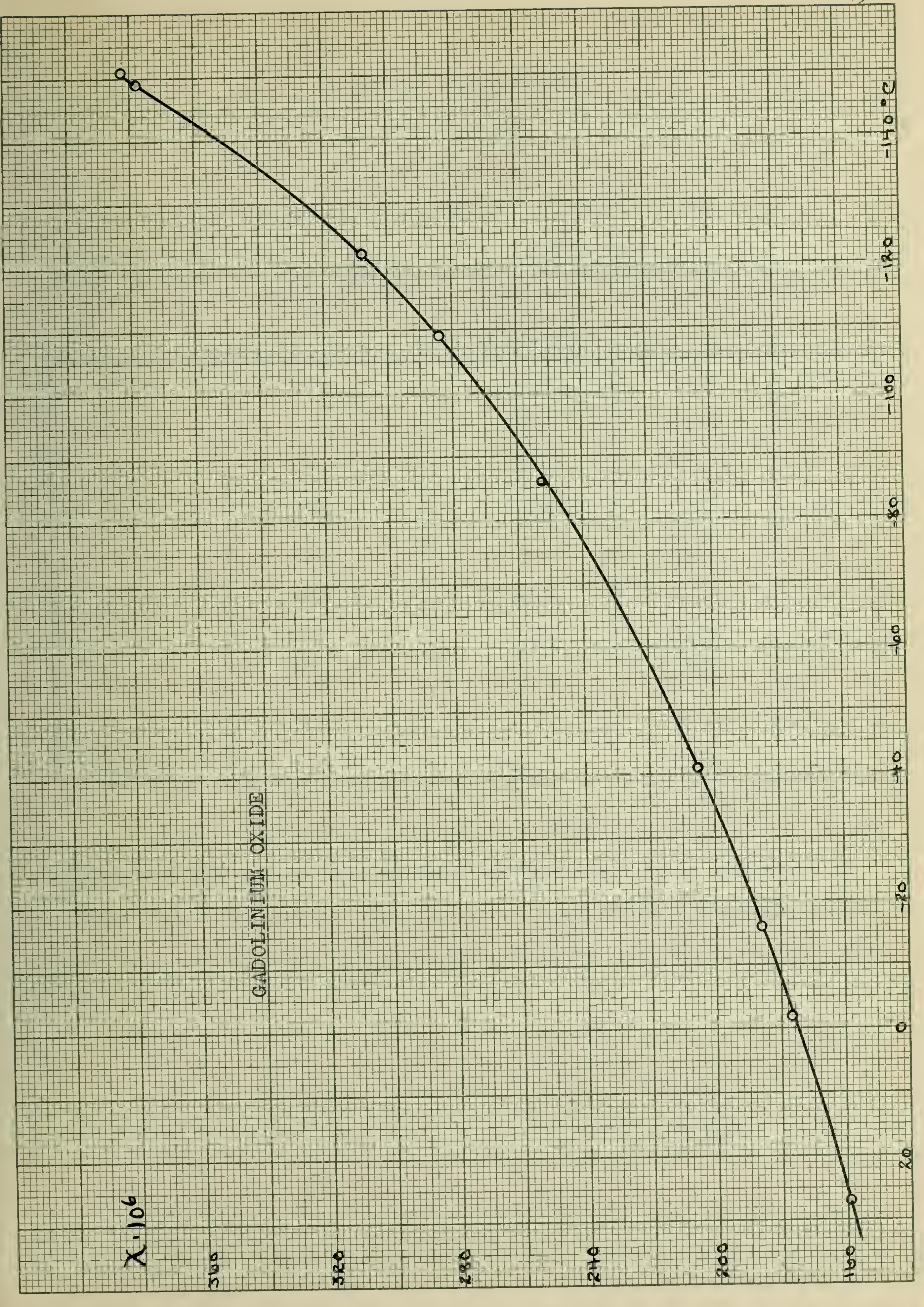

GADOLINIUM OXIDE
χ·10^6
360
320
280
240
200
160
-140 °C
-120
-100
-80
-60
-40
-20
0
20

Holmium Oxide (Ho_2O_3)

50% Holmium

50% Yttrium

Magnetizing Current 1 1/2 amperes   Weight 0.05446 g.

Correction -0.55 $\chi \cdot 10^6 = 18.80$ d.

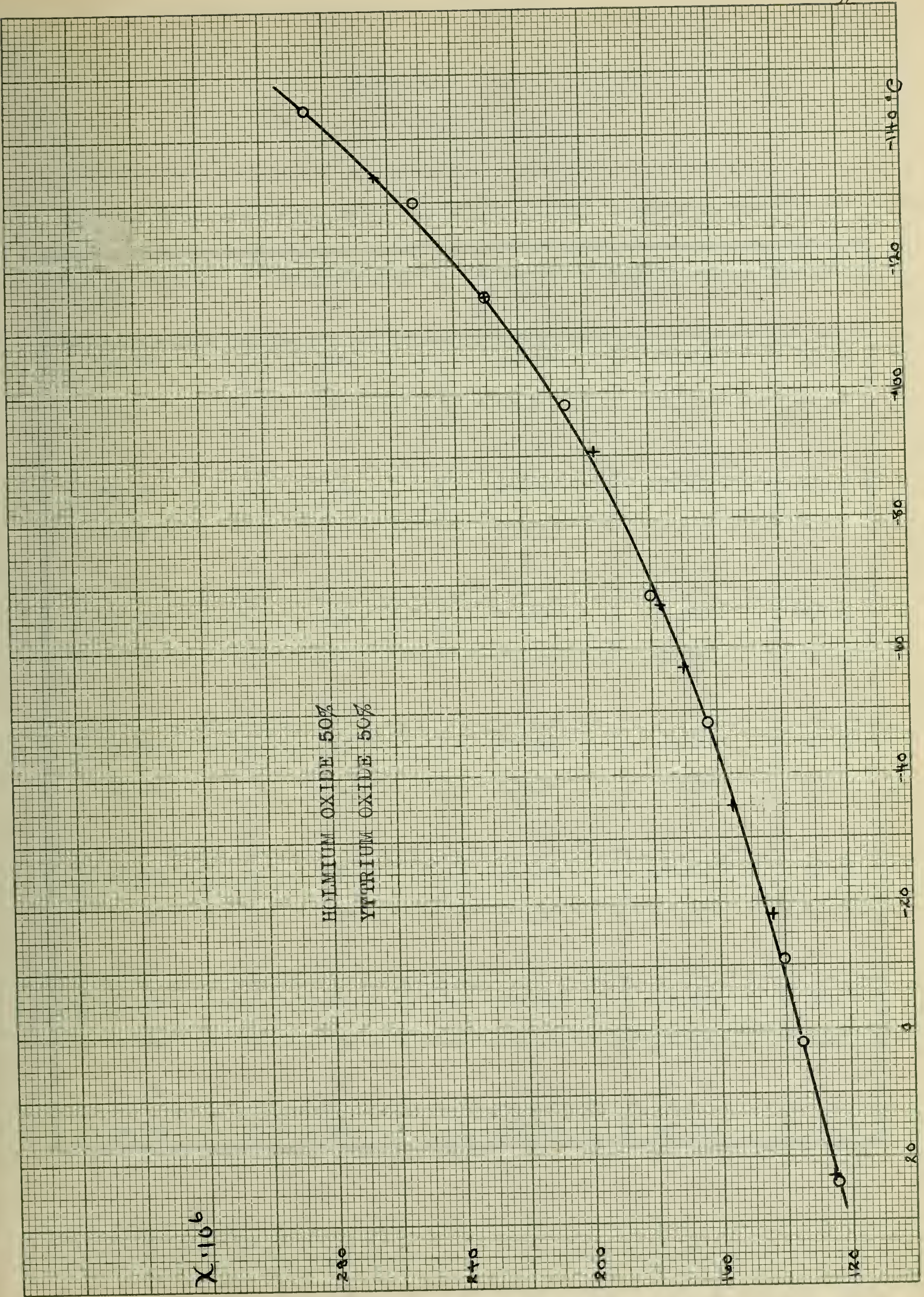
Thermocouple deflection	Temperature °C	Torsion balance deflection	Corrected deflection	$\chi \cdot 10^6$
-3.04	24	7.17	6.62	124.5
-0.20	2	7.73	7.18	135.0
+1.30	-11	8.00	7.45	140.0
5.11	-48	9.22	8.67	163.0
7.05	-68	10.12	9.57	179.9
5.98	-57	9.60	9.05	170.1
9.61	-98	11.51	10.96	206.0
10.98	-115	12.80	12.25	230.3
12.17	-130	13.96	13.41	252.1
13.36	-144.5	15.77	15.22	286.1

When the temperature reached -144.5 no more liquid air was added and the sample was allowed to heat up. This was done in order to be absolutely sure that the thermocouple actually measured the temperature of the sample and did not have an appreciable lag.

Sample heating.

Points indicated thus +

Thermocouple deflection	Temperature °C	Torsion balance deflection	Corrected deflection	$\chi \cdot 10^6$
13.36	-144.5	15.77	15.22	286.1
12.53	-134.5	14.62	14.07	264.5
11.05	-115	12.80	12.25	230.3
8.98	- 90.5	11.04	10.49	197.2
6.88	- 66.5	9.96	9.41	176.9
3.91	- 35	8.83	8.28	155.7
2.11	- 18	8.18	7.63	143.4
-2.89	+ 23	7.21	6.66	125.2


HOLMIUM OXIDE 50%
YTTRIUM OXIDE 50%
χ·10⁶
280
240
200
160
120
-140°C
-120
-100
-80
-60
-40
-20
0
20

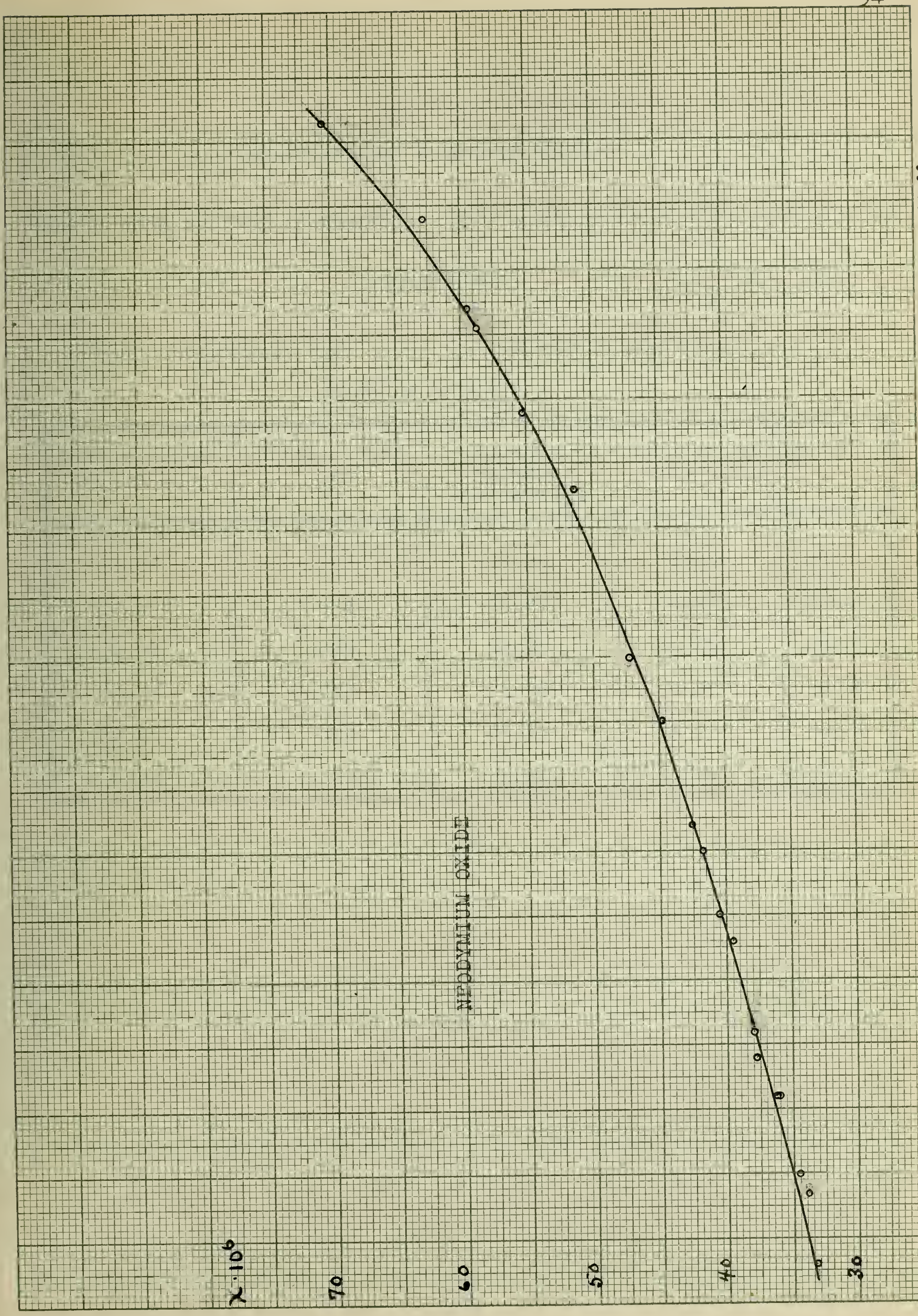
Neodymium Oxide (Nd_2O_3)

99 1/2% or better

Magnetizing Current 5 amperes   Weight 0.02204 g.

Correction -2.54 at 25°, -2.14 at -153°   Constant 4.385

Thermocouple deflection	Temperature °C	Torsion balance deflection	Corrected deflection	$\chi \cdot 10^6$
-3.15	25	10.13	7.59	33.3
-1.52	13	10.22	7.71	33.8
-1.11	10	10.36	7.86	34.5
+0.33	-2	10.74	8.26	36.2
0.35	-2	10.68	8.20	36.0
1.18	-8	11.05	8.61	37.8
1.44	-12	11.09	8.67	38.0
3.05	-26	11.40	9.01	39.5
3.42	-30	11.61	9.23	40.5
4.46	-40	11.84	9.48	41.6
4.89	-44	12.05	9.70	42.5
6.31	-60	12.52	10.20	44.7
7.22	-70	13.10	10.80	47.4
9.33	-96	13.97	11.72	51.4
10.51	-108	14.83	12.60	55.3
11.63	-121	15.58	13.38	58.7
11.83	-124	15.74	13.54	59.4
12.92	-138	16.52	14.34	62.9
14.10	-153	18.24	16.10	70.6


NEODYMIUM OXIDE
χ·10⁶
70
60
50
40
30
-140°C.
-120
-100
-80
-60
-40
-20
0
20

Ytterbium Oxide (Yb_2O_3)

Ytterbium and Lutecium Mixture

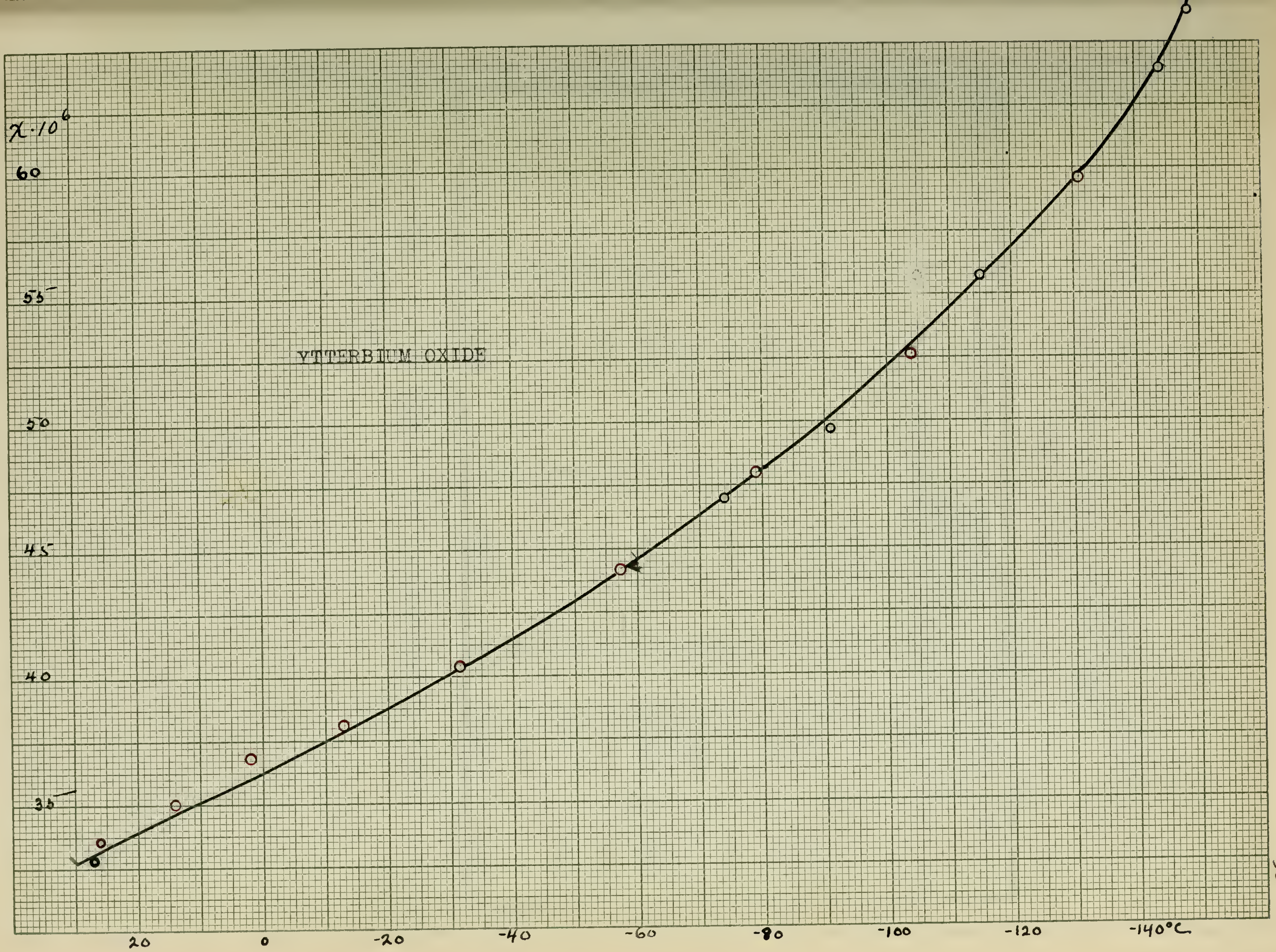
Magnetizing Current 5 amperes. Correction 2.54 at 27°, 2.14 at -150°

Sample No. 1

Points indicated thus o Weight 0.02140 g.

$\chi \cdot 10^6 = 4.512\ d$

Thermocouple deflection	Temperature °C	Torsion balance deflection	Corrected deflection	$\chi \cdot 10^6$
-3.45	+27	9.82	7.28	32.8
+7.61	-74	12.71	10.42	47.0
9.03	-91	13.29	11.03	49.8
11.02	-115	14.58	12.37	55.8
13.31	-144	16.37	14.19	64.0
13.65	-148.5	16.90	14.76	66.6


YTTERBIUM OXIDE
χ·10⁶
60
55
50
45
40
35
20
0
-20
-40
-60
-80
-100
-120
-140°C

Sample No. 2

Points indicated thus o Weight 0.02950 g.

*Zero correction 2.17 at 26°, 1.65 at -153°C

$\chi \cdot 10^6 = 3.273$ d

Thermocouple deflection	Temperature °C	Torsion balance deflection	Corrected deflection	$\chi \cdot 10^6$
-3.30	26	12.46	10.29	33.7
-1.75	14	12.85	10.68	35.0
+0.25	-2	13.44	11.27	36.9
1.56	-13	13.82	11.65	38.1
3.49	-31.5	14.52	12.35	40.4
6.03	-57.5	15.69	13.52	44.3
8.02	-79	16.83	14.66	48.0
10.08	-104	18.18	16.08	52.6
12.22	-131	20.22	18.22	59.6
13.99	-153	23.04	21.39	70.0
14.02	-153	23.06	21.41	70.1

* Correction not the same as for first sample on account of minor changes in apparatus

VI DISCUSSION OF RESULTS

None of the materials investigated follow Curie's law which states that the susceptibility of paramagnetic bodies times the absolute temperature is equal to a constant: (χT = Const.) However, they were all found to follow a modification of Curie's law: that is, the susceptibility times the absolute temperature plus a constant was equal to a constant, $\chi(T+\theta)=C$. This constant is quite different for the various materials. It was determined as follows:

Take the equation

$$\chi(T+\theta) = C$$

Multiplying out we have

$$\chi T + \theta\chi = C.$$

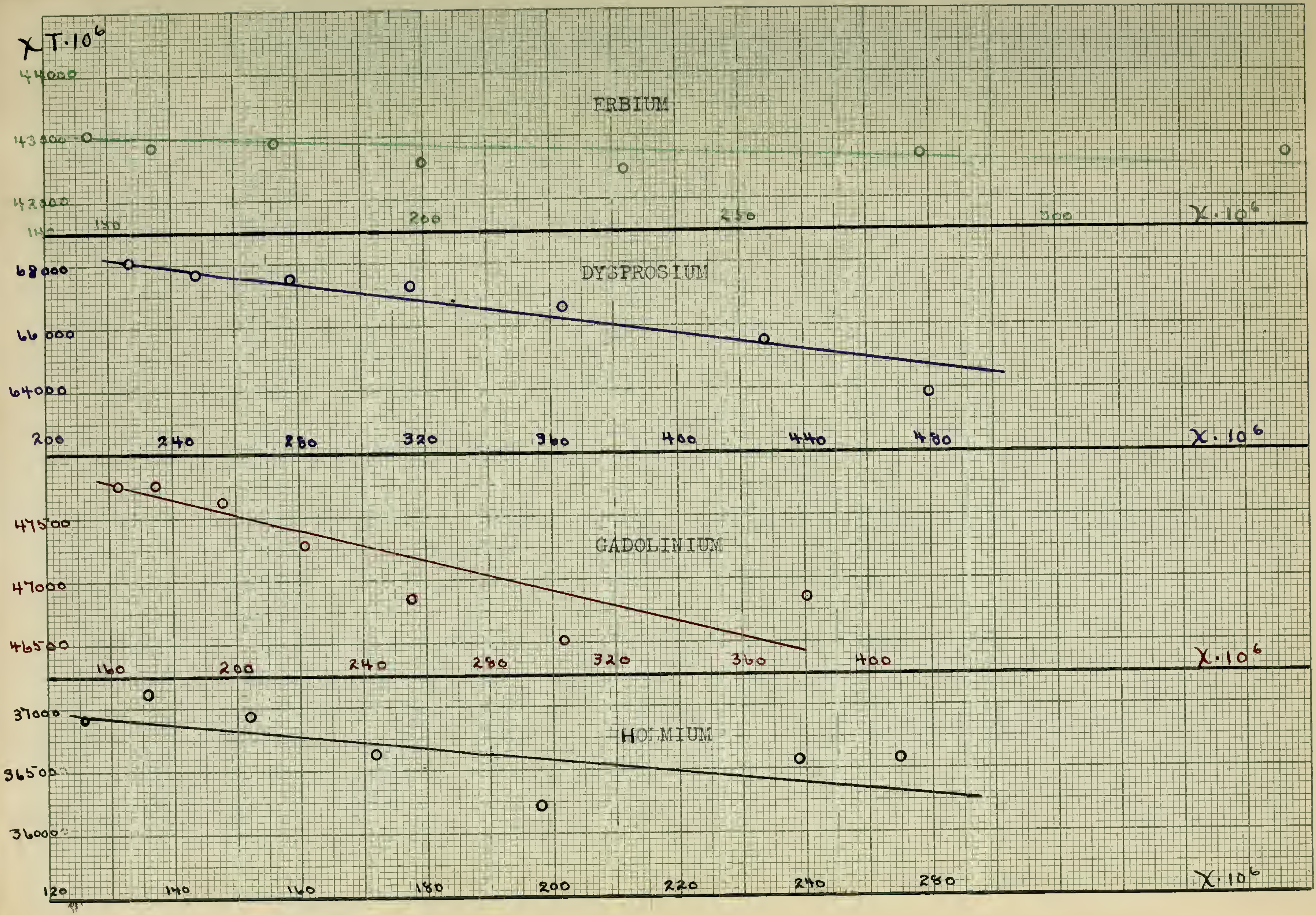
Now, if χT is considered as a new variable, say z, then the equation

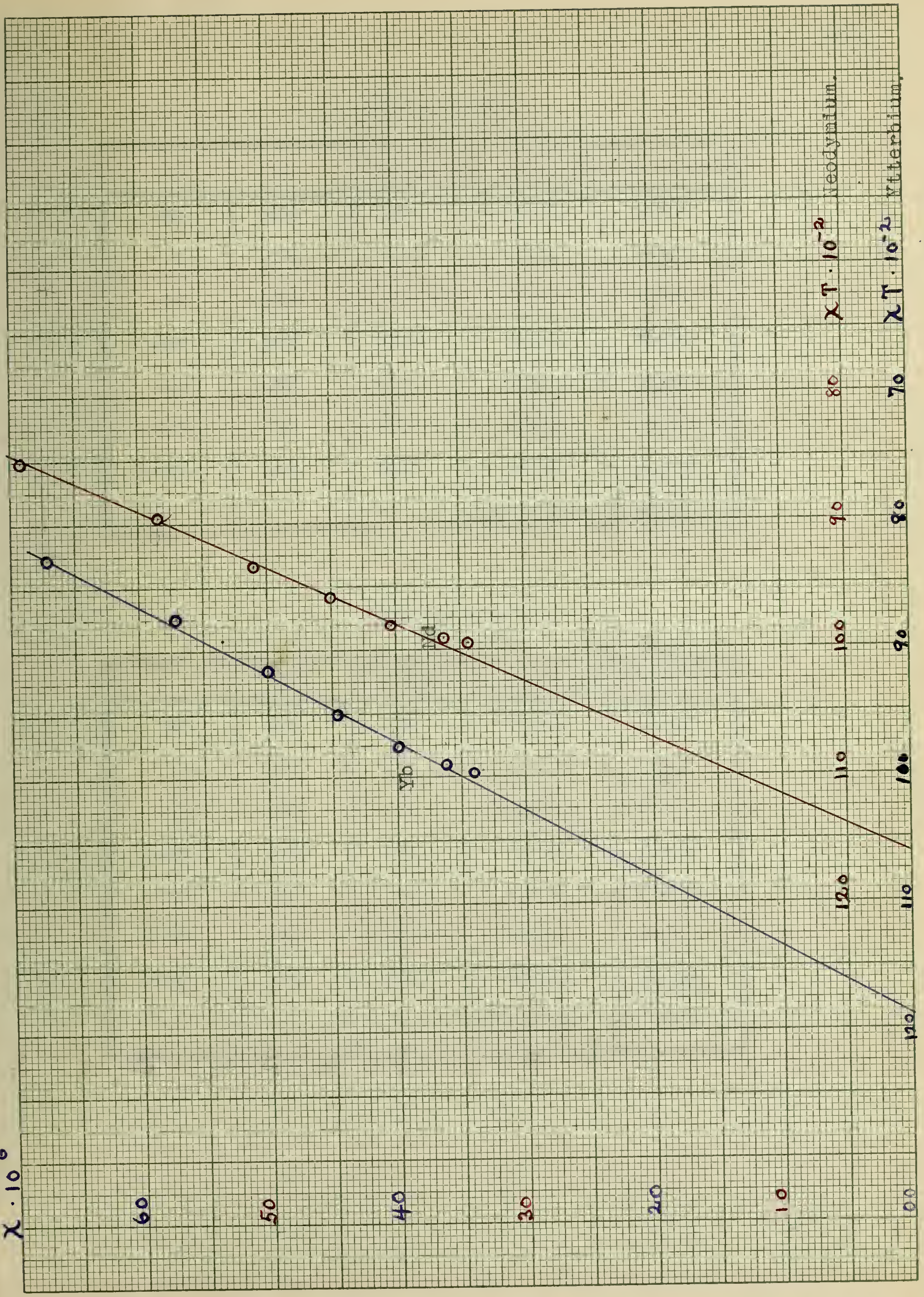
$$z + \theta\chi = C,$$

is a linear one and θ represent the slope of the straight line.

In obtaining the data for these straight lines, the values for the susceptibilities and the temperatures were taken from the curves giving the variation of χ with the temperature.

The points at first sight may not seem to lie as closely to the line as might be expected. This is not the case. Take for example Gadolinium oxide. The lower points seem to lie wide from the straight line. If, however, an error as small as one per cent is assumed in the product χ T which contains two quantities experimentally determined, then all the points will be brought on the line. The values of θ taken from the curves are erbium


χT·10^6
ERBIUM
44000
43000
42000
140
150
200
250
300
χ·10^6
DYSPROSIUM
68000
66000
64000
200
240
280
320
360
400
440
480
χ·10^6
GADOLINIUM
47500
47000
46500
160
200
240
280
320
360
400
χ·10^6
HOLMIUM
37000
36500
36000
120
140
160
180
200
220
240
280
χ·10^6


χ · 10^6
60
50
40
30
20
10
00
χT · 10^-2 Neodymium.
80
90
100
110
120
χT · 10^-2 Ytterbium.
70
80
90
100
110
120
Nd
Yb

Erbium Oxide

t	T	$\chi \cdot 10^6$	$\chi \cdot T \cdot 10^6$	$\chi \cdot (T+3) 10^6$
20	293	147	43070	43510
0	273	157	42860	43330
-30	243	176.5	42890	43420
-60	213	200	42600	43200
-90	183	232	42460	43150
-120	153	279	42690	43520
-150	123	347	42680	43720
			Average	43410

Holmium Oxide

t	T	$\chi \cdot 10^6$	$\chi \cdot T \cdot 10^6$	$\chi \cdot 10^6 (T+50°)$
20	293	126	36920	37550
0	273	136	37130	37810
-30	243	152	36940	37700
-60	213	172	36640	37500
-90	183	198	36230	37220
-120	153	239	36570	37760
-140	133	275	36580	37950
			Average	37640

Gadolinium Oxide

t	T	$\chi \cdot 10^6$	$\chi \cdot T \cdot 10^6$	$\chi \cdot (T+6) \cdot 10^6$
20	293	163	47760	48740
0	273	175	47780	48830
-30	243	196	47630	48800
-60	213	222	47290	48620
-90	183	256	46850	48380
-120	153	304	46510	48340
-150	123	381	46860	49150
			Average	48700

Dysprosium Oxide

t	T	$\chi \cdot 10^6$	$\chi \cdot T \cdot 10^6$	$\chi \cdot (T+13.5) \cdot 10^6$
27	300	227	68100	71160
0	273	248	67700	71050
-30	243	278	67550	71310
-60	213	316	67310	71570
-90	183	364	66610	71530
-120	153	428	65480	71260
-140	133	480	63840	70320
			Average	71130

Neodymium Oxide

t	T	$\chi\cdot10^6$	$\chi T\cdot10^6$	$\chi(T+45)10^6$
25	298	33.4	9953	11460
0	273	36.3	9910	11540
-30	243	40.4	9817	11640
-60	213	45	9585	11610
-90	183	51	9333	11630
-120	153	58.5	8951	11580
-150	123	69.2	8512	11630
			Average	11584

Ytterbium Oxide

t	T	$\chi\cdot10^6$	$\chi T\cdot10^6$	$\chi(T+51)10^6$
20	293	34	9962	11800
0	273	36.25	9896	11850
-30	243	40.1	9744	11910
-60	213	44.6	9500	11910
-90	183	50	9150	11850
-120	153	57.1	8736	11820
-150	123	67.25	8270	11900
			Average	11862

oxide 3°, Holmium oxide 5°, Gadolinium oxide 6°, Dysprosium oxide 13.5°, Neodymium oxide 45°, Ytterbium oxide 51°.

One explanation of this deviation from Curie's law is found by considerations of zero point energy. Einstein and Stern[1] from considerations of the work by Euchen on the specific heat of hydrogen take the rotational energy of the molecules at any temperature as

$$U = \frac{h\nu}{e^{\frac{h\nu}{kT}} - 1} + \frac{1}{2}h\nu$$

where h and k are Planck's constants and ν is the frequency of the rotation. Oosterhuis[2] places $\frac{1}{\chi}$ proportional to this value of U. This gives directly $\chi(T + \theta) = C$ where $\theta = \frac{1}{6}\frac{h\nu_0}{k}$.

Since $\nu_0 = \frac{h}{4\pi I}$ where I is the moment of inertia of the molecule, he concludes that molecules with small moments of inertia have a large value of θ and hence a large zero point energy $(\frac{1}{2}h\nu_0)$. In other words, molecules having large moments of inertia, such for instance as those containing large amounts of water of crystallization, would not be expected to deviate markedly from Curie's law.

Starting from an entirely different standpoint Dr. Kunz[3] of this laboratory has derived an expression for the same law. He reasons that since it is quite likely that the electrons responsible for the paramagnetism revolve in the outer layer of the atom, in this case the molecular moment would be the resultant of all the atomic moments in the molecule. Hence, since it is

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[1] Ann. d. Physik, 40, 551 (1913)

[2] Phys. Zeit., 14, 862 (1913)

[3] Phys. Rev. (2), 6, 113 (1915)

quite probable that some portion of the kinetic energy due to temperature is carried by the atoms, a change in the temperature would affect the resultant moment. Therefore, we can say

$$M = M_o\, f(T)$$

In the same way the forces which oppose the tendency of the external field to line up the elementary magnets is composed of the temperature agitation (RT) plus a term due to the influence of the mutual effect of the molecules on one another. This would be a certain function of the temperature $f_1(T)$. The above leads to the intensity of magnetization $(\mathfrak{I})$ is equal to

$$\left[M_o \cdot f(T)\right]^2 \frac{HN}{3[RT + f_1(T)]}$$

where H is the external field and N the number of molecules per unit volume. This gives

$$\chi = \frac{M_o f(T)^{2}}{3[RT + f_1(T)]}$$

If $f(T)$ is equal to 1 and $f_1(T)$ is equal to $3\theta R$, then

$$\chi = \frac{M_o^2}{3(RT + \theta R)}$$

or $$\chi(T + \theta) = \text{const.}$$

This theory like that of Oosterhuis will not only account for this modification of Curie's law but will also account for the temperature variation on the three general classes into which the materials investigated at Onnes' laboratory fall.* The

---

*1 Substances which follow Curie's law to liquid hydrogen temperatures below which χT is too small.

2 Substances which obey $\chi(T+\theta)=C$ down to liquid hydrogen temperature below which it does not.

3 Substances which change very little with temperature and which in the range liquid nitrogen to liquid hydrogen are almost constant.

only necessary condition is that the proper functions be selected for f(T) and $f_1(T)$.

The table gives the value of χ for the oxides investigated for a temperature of 20°C and the corresponding values as determined by Urbain and Jansch[1].

Oxide	Atomic Weight	$\chi \cdot 10^6$	θ	$\chi \cdot 10^6$ Urbain
Ytterbium and Lutecium	172 ±.1 174 ±.5	34	51	---
Dysprosium	162.5±.5	294 ?	17	290
Neodymium	144.3±.5	34	45	33.5
Gadolinium	157.3±.2	163	6	161
Holmium	163.5?	252 ?	10	---
Erbium	167.7±.2	155 ?	3	---

The ytterbium sample was a mixture of ytterbium and lutecium. The dysprosium sample was not the one for which the temperature variation was determined but one used by Dr. Engle[2] of the chemistry department of the University of Illinois for atomic weight work. The neodymium was practically 100%. The gadolinium was about 97% but contained slight amounts of dysprosium and holmium with a trace of praseodymium. Since these impurities would raise the value of χ, the value as measured, it was not thought necessary to correct. Holmium was 50% with 50% yttrium and less than 0.5% dysprosium. The value given in the table is the value determined (126) multiplied by 2. The yttrium

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[1] Urbain and Jansch. Comp. rend. 146, 922 (1908.

[2] Doctor's Thesis (1916). Dr. Engle finds the atomic weight of this sample to be 164.35

content has no appreciable effect on χ (for yttrium=-0.14×10^{-6}). The erbium was 95% pure with 5% yttrium, and the value given in the table calculated on a basis of 100%. In a similar manner the values of θ are calculated from the observed values, the only exception being dysprosium. The small value 232.5 obtained for the sample whose temperature variation was studied made it appear to be only 79% pure. Applying this correction to the sample in question the value of θ changes from 13.5° to 17°.*

The absolute value for χ as measured is thought to be within 1 1/2% of the truth. The principal error enters in the determination of $\frac{\Delta H}{\Delta x}$ due to the difficulty in reading Δx with sufficient accuracy.

It is interesting to plot the susceptibility and the value of θ against atomic weight. The atomic weights are plotted as lines instead of points with the length of the line indicating the uncertainty in the atomic weight. The curves are both of a broken type, the χ curve showing a minimum at samarium and a maximum at dysprosium. Between points of maximum and minimum an almost linear relation exists and it seems very probable that the value of thulium oxide at 20°C (which has never been determined) is about $140 \cdot 10^{-6}$ From the marked chemical similarity of the rare earths one would expect that the moment of inertia of the molecule would increase with the atomic weight and therefore, according to Oosterhuis the value of θ should decrease. Such is not found to be the case.

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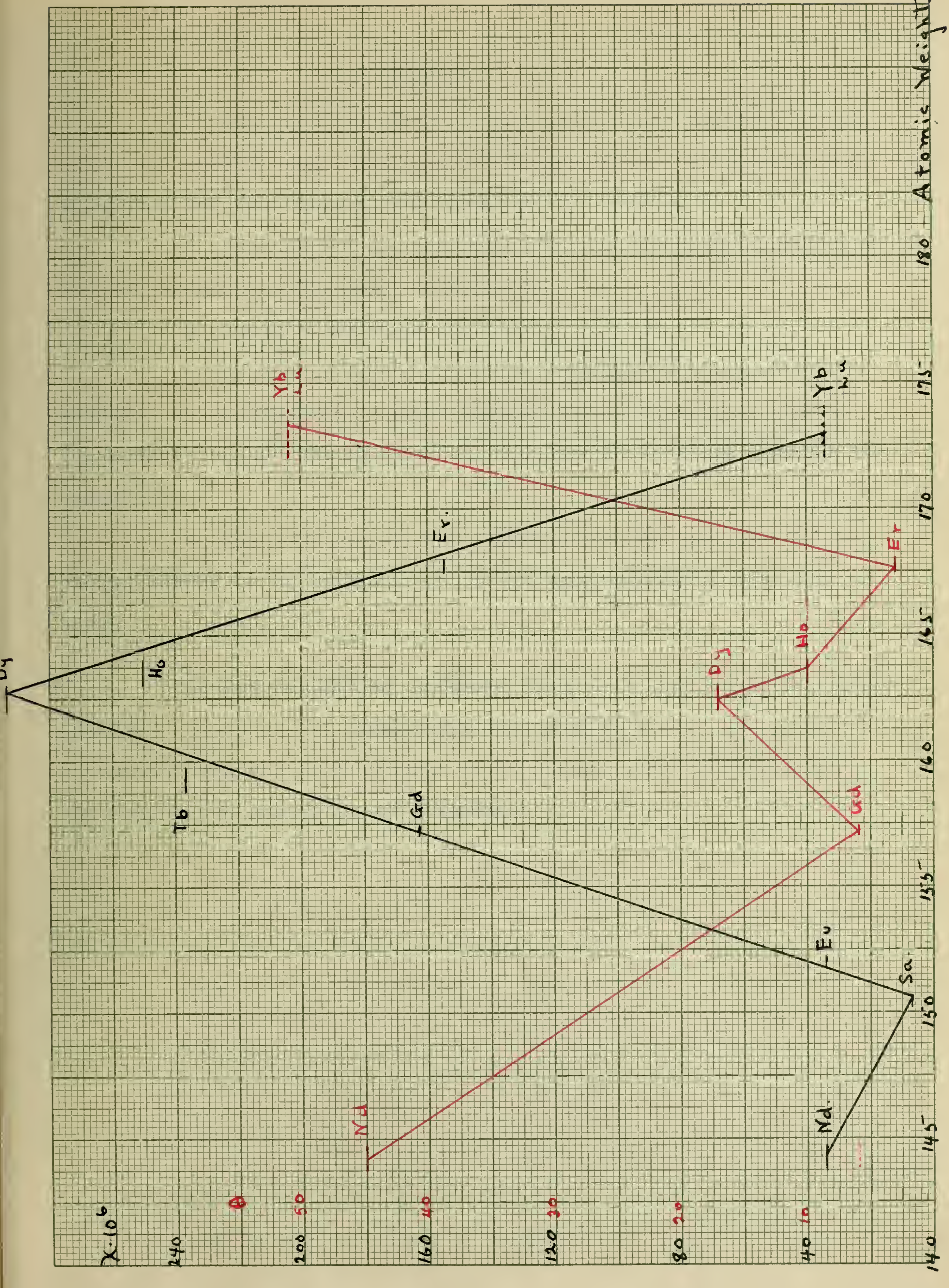
* Onnes and Oosterhuis obtain a value of 16 for this constant


X·10^6
240
200
160
120
80
40
θ
50
40
30
20
10
140
145
150
155
160
165
170
175
180
Atomic Weight
Nd
Sa
Eu
Gd
Tb
Dy
Ho
Er
Yb
Lu
Nd
Gd
Dy
Ho
Er
Yb
Lu

VII SUMMARY

1 The mass susceptibilities have been measured for the oxides of erbium, gadolinium, holmium, neodymium, dysprosium and ytterbium for the temperature range 20° to -150°C.

2 The results can be expressed by the formula $\chi(T+\theta)=C$ and the constant θ has been determined.

3 Curie's law does not hold.

4 As far as Curie's law is essential for the determination of the magneton, these measurements are unfavorable to the conception but not necessarily conclusive evidence against the magneton.

5 The laws can be explained either by the zero point energy theory of Oosterhuis, or by the agglomeration theory of Kunz.

It now becomes my pleasant duty to acknowledge my indebtedness to Dr. Kunz for suggesting the problem and for help in this investigation, and to Professor A. P. Carman for his advice and the facilities placed at my disposal.

VITA

Oscar Alan Randolph was born in Summersville, Missouri, November 25, 1886. He received his early education in the public schools of Kansas City, Missouri, and graduated from the Kansas City (Missouri) Central High School in 1907. He entered the Missouri School of Mines in the fall of 1907 and received the Bachelor of Science degree in Metallurgy from this institution in 1911. During 1910-1911 he was a student assistant in chemistry at the Missouri School of Mines. From 1911 to 1916 he served as assistant in physics at the University of Illinois, receiving the degree of Master of Science in 1913.